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Publication date:
2007

Document Version
Publisher's PDF, also known as Version of record

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Anna Dall'Acqua, Thomas Østergaard Sørensen and Edgardo Stockmeyer

R-2007-17

August 2007

Department of Mathematical Sciences
Aalborg University
Fredrik Bajers Vej 7 G ▪ DK - 9220 Aalborg Øst ▪ Denmark
Phone: +45 96 35 80 80 ▪ Telefax: +45 98 15 81 29
URL: www.math.auc.dk/research/reports/reports.htm

ISSN 1399–2503 ▪ On-line version ISSN 1601–7811

HARTREE-FOCK THEORY FOR PSEUDORELATIVISTIC ATOMS

ANNA DALL'ACQUA, THOMAS ØSTERGAARD SØRENSEN, AND EDGARDO STOCKMEYER

Abstract. We study the Hartree-Fock model for pseudorelativistic atoms, that is, atoms where the kinetic energy of the electrons is given by the pseudo-relativistic operator $\sqrt{(|\mathbf{p}|c)^2+(mc^2)^2}-mc^2$. We prove the existence of a Hartree-Fock minimizer, and prove regularity away from the nucleus and point-wise exponential decay of the corresponding orbitals.

1. Introduction and results

We consider a model for an atom with N electrons and nuclear charge Z, where the kinetic energy of the electrons is described by the expression $\sqrt{(|\mathbf{p}|c)^2+(mc^2)^2}-mc^2$. This model takes into account some (kinematic) relativistic effects; in units where $\hbar=e=m=1$, the Hamiltonian becomes

$$\begin{aligned} H = H_{\mathrm{rel}}(N,Z,\alpha) &= \sum_{j=1}^{N}\Big\{\sqrt{-\alpha^{-2}\Delta_j+\alpha^{-4}}-\alpha^{-2}-\frac{Z}{|\mathbf{x}_j|}\Big\}+\sum_{1\le i<j\le N}\frac{1}{|\mathbf{x}_i-\mathbf{x}_j|} \\ &= \sum_{j=1}^{N}\alpha^{-1}\Big\{T(-\mathrm{i}\nabla_j)-V(\mathbf{x}_j)\Big\}+\sum_{1\le i<j\le N}\frac{1}{|\mathbf{x}_i-\mathbf{x}_j|}\,, \end{aligned} \tag{1}$$

with $T(\mathbf{p})=E(\mathbf{p})-\alpha^{-1}=\sqrt{|\mathbf{p}|^2+\alpha^{-2}}-\alpha^{-1}$ and $V(\mathbf{x})=Z\alpha/|\mathbf{x}|$. Here, α is Sommerfeld's fine structure constant; physically, $\alpha\simeq 1/137.036$.

The operator H acts on a dense subspace of the N-particle Hilbert space $\mathcal{H}_F=\wedge_{i=1}^{N}L^2(\mathbb{R}^3;\mathbb{C}^q)$ of antisymmetric functions, where q is the number of spin states. It is bounded from below on this subspace (more details below).

The *(quantum) ground state energy* is the infimum of the spectrum of H considered as an operator acting on $\mathcal{H}_F$:

$$E^{\mathrm{QM}}(N,Z,\alpha):=\inf\sigma_{\mathcal{H}_F}(H)=\inf\{\,\mathfrak{q}(\Psi,\Psi)\,|\,\Psi\in\mathcal{Q}(H),\langle\Psi,\Psi\rangle=1\}\,,$$

where $\mathfrak{q}$ is the quadratic form defined by H, and $\mathcal{Q}$ the corresponding form domain (see below); $\langle\ ,\ \rangle$ is the scalar product in $\mathcal{H}_F\subset L^2(\mathbb{R}^{3N};\mathbb{C}^{q^N})$.

In the Hartree-Fock approximation, instead of minimizing the functional $\mathfrak{q}$ in the entire N-particle space $\mathcal{H}_F$, one restricts to wavefunctions Ψ which are pure wedge products, also called Slater determinants:

$$\Psi(\mathbf{x}_1,\sigma_1;\mathbf{x}_2,\sigma_2;\dots;\mathbf{x}_N,\sigma_N)=\frac{1}{\sqrt{N!}}\,\det(u_i(\mathbf{x}_j,\sigma_j))_{i,j=1}^{N}\,, \tag{2}$$

with $\{u_i\}_{i=1}^N$ orthonormal in $L^2(\mathbb{R}^3;\mathbb{C}^q)$ (called *orbitals*). Notice that this way, $\Psi\in\mathcal{H}_F$ and $\|\Psi\|_{L^2(\mathbb{R}^{3N};\mathbb{C}^{q^N})}=1$.

Date: August 7, 2007.

The *Hartree-Fock ground state energy* is the infimum of the quadratic form $\mathfrak{q}$ defined by H over such Slater determinants:

$$E^{\mathrm{HF}}(N, Z, \alpha) := \inf\{\, \mathfrak{q}(\Psi, \Psi) \,|\, \Psi \text{ Slater determinant}\}\,. \tag{3}$$

For the non-relativistic Hamiltonian,

$$H_{\mathrm{cl}}(N, Z) = \sum_{j=1}^{N} \Big\{ -\frac{1}{2}\Delta_j - \frac{Z}{|\mathbf{x}_j|} \Big\} + \sum_{1 \le i < j \le N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}\,, \tag{4}$$

the mathematical theory of this approximation has been much studied, the ground-breaking work being that of Lieb and Simon [13]; see also [15] for work on excited states. For a comprehensive discussion of Hartree-Fock (and other) approximations in quantum chemistry, and an extensive literature list, we refer to [10].

The aim of the present paper is to study the Hartree-Fock approximation for the pseudorelativistic operator H in (1).

We turn to the precise description of the problem. The one-particle operator $h_0 = T(-\mathrm{i}\nabla) - V(\mathbf{x})$ is bounded from below (by $\alpha^{-1}[(1-(\pi Z\alpha/2)^2)^{1/2}-1]$) if and only if $Z\alpha \le 2/\pi$ (see [7], [9, 5.33 p. 307], and [25]; we shall have nothing further to say on the critical case $Z\alpha = 2/\pi$). More precisely, if $Z\alpha < 1/2$, then V is a small *operator* pertubation of T. In fact [7, Theorem 2.1 c)], $\big\| |\mathbf{x}|^{-1}(T(-\mathrm{i}\nabla)+1)^{-1} \big\|_{\mathcal{B}(L^2(\mathbb{R}^3))} = 2$. As a consequence, h_0 is selfadjoint with $\mathcal{D}(h_0) = H^1(\mathbb{R}^3;\mathbb{C}^q)$ when $Z\alpha < 1/2$. It is essentially selfadjoint on $C_0^\infty(\mathbb{R}^3;\mathbb{C}^q)$ when $Z\alpha \le 1/2$.

If, on the other hand, $1/2 \le Z\alpha < 2/\pi$, then V is only a small *form* pertubation of T: Indeed [9, 5.33 p. 307],

$$\int_{\mathbb{R}^3} \frac{|f(\mathbf{x})|^2}{|\mathbf{x}|}\, d\mathbf{x} \le \frac{\pi}{2} \int_{\mathbb{R}^3} |\mathbf{p}||\hat{f}(\mathbf{p})|^2\, d\mathbf{p} \quad \text{for} \quad f \in H^{1/2}(\mathbb{R}^3)\,, \tag{5}$$

where $\hat{f}$ denotes the Fourier transform of f. Hence, the quadratic form $\mathfrak{v}$ given by

$$\mathfrak{v}[u, v] := (V^{1/2}u, V^{1/2}v) \quad \text{for} \quad u, v \in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q) \tag{6}$$

(multiplication by $V^{1/2}$ in each component) is well defined (for all values of $Z\alpha$). Here, $(\ ,\ )$ denotes the scalar product in $L^2(\mathbb{R}^3;\mathbb{C}^q)$. Let $\mathfrak{e}$ be the quadratic form with domain $H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)$ given by

$$\mathfrak{e}[u, v] := (E(\mathbf{p})^{1/2}u, E(\mathbf{p})^{1/2}v) \quad \text{for} \quad u, v \in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,. \tag{7}$$

By abuse of notation, we write $E(\mathbf{p})$ for the (strictly positive) operator $E(-\mathrm{i}\nabla) = \sqrt{-\Delta + \alpha^{-2}}$. Then, using (5) and that $|\mathbf{p}| \le E(\mathbf{p})$,

$$\mathfrak{v}[u, u] \le Z\alpha\frac{\pi}{2}\,\mathfrak{e}[u, u] \quad \text{for} \quad u \in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q) \setminus \{0\}\,. \tag{8}$$

Hence, by the KLMN theorem [18, Theorem X.17], if $Z\alpha < 2/\pi$ there exists a unique self-adjoint operator h_0 whose quadratic form domain is $H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)$ such that (with $\mathfrak{t} = \mathfrak{e} - \alpha^{-1}$)

$$(u, h_0 v) = \mathfrak{t}[u, v] - \mathfrak{v}[u, v] \quad \text{for} \quad u, v \in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,, \tag{9}$$

and h_0 is bounded below by $-\alpha^{-1}$. Moreover, if $Z\alpha < 2/\pi$ then the spectrum of h_0 is discrete in $[-\alpha^{-1}, 0)$ and absolutely continuous in $[0, \infty)$ [7, Theorems 2.2 and 2.3].

As for the N-particle operator in (1), when $Z\alpha < 2/\pi$, (5) implies that the quadratic form

$$\mathfrak{q}(\Psi,\Phi) = \sum_{j=1}^{N}\Big\{\langle\, E(\mathbf{p}_j)^{1/2}\Psi, E(\mathbf{p}_j)^{1/2}\Phi\,\rangle - \alpha^{-1}\langle\Psi,\Phi\rangle - \langle\, V(\mathbf{x}_j)^{1/2}\Psi, V(\mathbf{x}_j)^{1/2}\Phi\,\rangle\Big\}$$

$$+ \sum_{1\le i<j\le N}\langle\,|\mathbf{x}_i-\mathbf{x}_j|^{-1/2}\Psi, |\mathbf{x}_i-\mathbf{x}_j|^{-1/2}\Phi\rangle\ ,\quad \Psi,\Phi\in\bigwedge_{i=1}^{N}H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,,$$

is well-defined, closed, and bounded from below. The operator H can then be defined as the corresponding (unique) self-adjoint operator. It satisfies

$$\bigwedge_{i=1}^{N}H^{1}(\mathbb{R}^3;\mathbb{C}^q)\subset\mathcal{D}(H)\subset\mathcal{Q}(H)=\bigwedge_{i=1}^{N}H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,,$$
$$\mathfrak{q}(\Psi,\Phi)=\langle\Psi,H\Phi\rangle\,,\quad \Phi\in\mathcal{D}(H)\,,\quad \Psi\in\mathcal{Q}(H)\,.$$

For $Z\alpha < 1/2$, $\mathcal{D}(H) = \wedge_{i=1}^{N}H^1(\mathbb{R}^3;\mathbb{C}^q)$. All this follows from (the statements and proofs of) [18, Theorem X.17] and [17, Theorem VIII.15]. See [14] for further references on H. We shall not have anything further to say on H in this paper, however, but will only study the Hartree-Fock problem mentioned above. We now discuss this in more detail.

It is convenient to use the one-to-one correspondence between Slater determinants and projections onto finite dimensional subspaces of $L^2(\mathbb{R}^3;\mathbb{C}^q)$. Indeed, if Ψ is given by (2) with $\{u_i\}_{i=1}^N\subset H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)$, orthonormal in $L^2(\mathbb{R}^3;\mathbb{C}^q)$, and γ is the projection onto the subspace spanned by $u_1,\dots,u_N$, then the kernel of γ is given by

$$\gamma(\mathbf{x},\sigma;\mathbf{y},\tau)=\sum_{j=1}^{N}u_j(\mathbf{x},\sigma)\overline{u_j(\mathbf{y},\tau)}\,. \tag{10}$$

Let $\rho_\gamma\in L^1(\mathbb{R}^3)$ denote the 1-particle density associated to γ given by

$$\rho_\gamma(\mathbf{x})=\sum_{\sigma=1}^{q}\gamma(\mathbf{x},\sigma;\mathbf{x},\sigma)=\sum_{\sigma=1}^{q}\sum_{j=1}^{N}|u_j(\mathbf{x},\sigma)|^2\,.$$

Then the energy expectation of Ψ depends only on γ, more precisely,

$$\mathfrak{q}(\Psi,\Psi)=\langle\Psi,H\Psi\rangle=\mathcal{E}^{\mathrm{HF}}(\gamma)\,,$$

where $\mathcal{E}^{\mathrm{HF}}$ is the Hartree-Fock energy functional defined by

$$\mathcal{E}^{\mathrm{HF}}(\gamma)=\alpha^{-1}\big\{\,\mathrm{Tr}[E(\mathbf{p})\gamma]-\alpha^{-1}\,\mathrm{Tr}[\gamma]-\mathrm{Tr}[V\gamma]\big\}+\mathcal{D}(\gamma)-\mathcal{E}x(\gamma)\,. \tag{11}$$

Here,

$$\mathrm{Tr}[E(\mathbf{p})\gamma]:=\sum_{j=1}^{N}\mathfrak{e}[u_j,u_j]\ ,\quad \mathrm{Tr}[V\gamma]:=\sum_{j=1}^{N}\mathfrak{v}[u_j,u_j]=Z\alpha\int_{\mathbb{R}^3}\frac{\rho_\gamma(\mathbf{x})}{|\mathbf{x}|}\,d\mathbf{x}\,,$$

$\mathcal{D}(\gamma)$ is the *direct* Coulomb energy,

$$\mathcal{D}(\gamma)=\frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho_\gamma(\mathbf{x})\rho_\gamma(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}\,d\mathbf{y}\,, \tag{12}$$

and $\mathcal{E}x(\gamma)$ is the *exchange* Coulomb energy,

$$\mathcal{E}x(\gamma)=\frac{1}{2}\sum_{\sigma,\tau=1}^{q}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{|\gamma(\mathbf{x},\sigma;\mathbf{y},\tau)|^2}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}\,d\mathbf{y}\,.$$

This way,

$$
\begin{aligned}
&E^{\mathrm{HF}}(N,Z,\alpha) = \inf\{\,\mathcal{E}^{\mathrm{HF}}(\gamma)\,|\,\gamma\in\mathcal{P}\,\}\,, \qquad (13)\\
&\quad \mathcal{P} = \{\gamma : L^2(\mathbb{R}^3;\mathbb{C}^q)\to L^2(\mathbb{R}^3;\mathbb{C}^q)\,|\,\gamma \text{ projection onto } \mathrm{span}\{u_1,\dots,u_N\},\\
&\qquad\qquad u_i\in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q), (u_i,u_j)=\delta_{i,j}\}\,.
\end{aligned}
$$

(Notice that if one of the orbitals u_i of γ is not in $H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)$, then $\mathcal{E}^{\mathrm{HF}}(\gamma)=+\infty$ (since $Z\alpha<2/\pi$).)

We now extend the definition of the Hartree-Fock energy functional $\mathcal{E}^{\mathrm{HF}}$, in order to turn the minimization problem (13) (that is, (3)) into a convex problem.

A *density matrix* $\gamma : L^2(\mathbb{R}^3;\mathbb{C}^q)\to L^2(\mathbb{R}^3;\mathbb{C}^q)$ is a self-adjoint trace class operator that satisfies the operator inequality $0\le\gamma\le\mathrm{Id}$. A density matrix γ has the integral kernel

$$
\gamma(\mathbf{x},\sigma;\mathbf{y},\tau) = \sum_j \lambda_j u_j(\mathbf{x},\sigma)\overline{u_j(\mathbf{y},\tau)}\,, \qquad (14)
$$

where λ_j, u_j are the eigenvalues and corresponding eigenfunctions of γ. We choose the u_j's to be orthonormal in $L^2(\mathbb{R}^3;\mathbb{C}^q)$. As before, let $\rho_\gamma\in L^1(\mathbb{R}^3)$ denote the 1-particle density associated to γ given by

$$
\rho_\gamma(\mathbf{x}) = \sum_{\sigma=1}^{q}\sum_j \lambda_j\,|u_j(\mathbf{x},\sigma)|^2\,. \qquad (15)
$$

Define

$$
\mathcal{A} := \big\{\gamma \text{ density matrix } \big|\ \mathrm{Tr}\,\big[E(\mathbf{p})\gamma\big] < +\infty\,\big\}\,, \qquad (16)
$$

where, by definition, for γ written as in (14),

$$
\mathrm{Tr}[E(\mathbf{p})\gamma] := \sum_j \lambda_j\,\mathfrak{e}[u_j,u_j]\,. \qquad (17)
$$

Notice that if $\gamma\in\mathcal{A}$ then all the terms in $\mathcal{E}^{\mathrm{HF}}(\gamma)$ (see (11)) are finite. Indeed, for $\gamma\in\mathcal{A}$ and written as in (14),

$$
\mathrm{Tr}[V\gamma] := \sum_j \lambda_j\,\mathfrak{v}[u_j,u_j] = Z\alpha\int_{\mathbb{R}^3}\frac{\rho_\gamma(\mathbf{x})}{|\mathbf{x}|}\,d\mathbf{x} \qquad (18)
$$

is finite, due to (8). In particular,

$$
u_j\in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\subset L^3(\mathbb{R}^3;\mathbb{C}^q)\,, \qquad (19)
$$

the last inclusion by Sobolev's inequality [12, Theorem 8.4].

On the other hand, if $\gamma\in\mathcal{A}$ then

$$
\rho_\gamma\in L^1(\mathbb{R}^3)\cap L^{4/3}(\mathbb{R}^3)\,. \qquad (20)
$$

This follows from Daubechies' inequality, see [5, pp. 519–520]. By Hölder's inquality, $\rho_\gamma\in L^{6/5}(\mathbb{R}^3)$. The Hardy-Littlewood-Sobolev inequality [12, Theorem 4.3] then implies that $\mathcal{D}(\gamma)$ (see (12)) is finite. Finally, $\mathcal{E}x(\gamma)\le\mathcal{D}(\gamma)$, since

$$
\begin{aligned}
&\mathcal{D}(\gamma)-\mathcal{E}x(\gamma)\\
&\quad = \frac{1}{2}\sum_{i,j}\lambda_i\lambda_j\sum_{\sigma,\tau=1}^{q}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{|u_i(\mathbf{x},\sigma)u_j(\mathbf{y},\tau)-u_j(\mathbf{x},\sigma)u_i(\mathbf{y},\tau)|^2}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}d\mathbf{y}\ge 0\,.
\end{aligned}
$$

Therefore, $\mathcal{E}^{\mathrm{HF}}$ defined by (11) extends to $\gamma\in\mathcal{A}$. This way, with h_0 defined as in (9),

$$
\mathrm{Tr}[h_0\gamma] = \mathrm{Tr}[E(\mathbf{p})\gamma] - \alpha^{-1}\,\mathrm{Tr}[\gamma] - \mathrm{Tr}[V\gamma]\,,
$$

and so

$$\mathcal{E}^{\mathrm{HF}}(\gamma) = \alpha^{-1}\,\mathrm{Tr}[h_0\gamma] + \mathcal{D}(\gamma) - \mathcal{E}x(\gamma)\,,\ \gamma\in\mathcal{A}\,. \tag{21}$$

Consider $\gamma\in\mathcal{A}$ and define, with ρ_γ as in (15),

$$R_\gamma(\mathbf{x}) := \int_{\mathbb{R}^3} \frac{\rho_\gamma(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{y}\,. \tag{22}$$

We have that

$$R_\gamma \in L^\infty(\mathbb{R}^3)\cap L^3(\mathbb{R}^3)\,. \tag{23}$$

This follows from (8) (for L^∞), and (20) and the weak Young inequality [12, p. 107] (for L^3). Next, define the operator K_γ with integral kernel

$$K_\gamma(\mathbf{x},\sigma;\mathbf{y},\tau) := \frac{\gamma(\mathbf{x},\sigma;\mathbf{y},\tau)}{|\mathbf{x}-\mathbf{y}|}\,. \tag{24}$$

The operator K_γ is Hilbert-Schmidt; we prove this fact in Lemma 2 below.

Note that, using (14) and the Cauchy-Schwarz inequality, $(u, R_\gamma u) \geq (u, K_\gamma u)$ (multiplication by R_γ is in each component). Denote by $\mathfrak{b}_\gamma$ the (non-negative) quadratic form given by

$$\mathfrak{b}_\gamma[u,v] := \alpha(u, R_\gamma v) - \alpha(u, K_\gamma v) \ \text{ for } \ u,v\in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,.$$

Then, using $(u, K_\gamma u)\geq 0$ and (8),

$$0 \leq \mathfrak{b}_\gamma[u,u] \leq \alpha(u, R_\gamma u) = \alpha\sum_{\sigma=1}^{q}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho_\gamma(\mathbf{y})|u(\mathbf{x},\sigma)|^2}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}\,d\mathbf{y} \leq \alpha\frac{2}{\pi}\,\mathrm{Tr}[\gamma]\,\mathfrak{e}[u,u]\,.$$

Therefore (by the statements and proofs of [18, Theorem X.17] and [17, Theorem VIII.15]), there exists a unique self-adjoint operator h_γ (called the *Hartree-Fock operator associated to* γ), which is bounded below (by $-\alpha^{-1}$), with quadratic form domain $H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)$ and such that

$$(u, h_\gamma v) = \mathfrak{t}[u,v] - \mathfrak{v}[u,v] + \mathfrak{b}_\gamma[u,v] \ \text{ for } \ u,v\in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,. \tag{25}$$

The operator h_γ has infinitely many eigenvalues in $[-\alpha^{-1},0)$ (when $N<Z$), and $\sigma_{\mathrm{ess}}(h_\gamma) = [0,\infty)$; both of these facts will be proved in Lemma 2 below.

The main result of this paper is the following theorem.

Theorem 1. *Let $Z\alpha < 2/\pi$, and let $N\geq 2$ be a positive integer such that $N < Z+1$.*

Then there exists an N-dimensional projection $\gamma^{\mathrm{HF}} = \gamma^{\mathrm{HF}}(N,Z,\alpha)$ minimizing the Hartree-Fock energy functional $\mathcal{E}^{\mathrm{HF}}$ given by (11)*, that is, $E^{\mathrm{HF}}(N,Z,\alpha)$ in* (13) *(and therefore, in* (3)*) is attained. In fact,*

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) = E^{\mathrm{HF}}(N,Z,\alpha) &= \inf\big\{\mathcal{E}^{\mathrm{HF}}(\gamma)\,\big|\,\gamma\in\mathcal{A}, \gamma^2=\gamma, \mathrm{Tr}[\gamma]=N\big\}\\ &= \inf\big\{\mathcal{E}^{\mathrm{HF}}(\gamma)\,\big|\,\gamma\in\mathcal{A},\ \mathrm{Tr}[\gamma]=N\big\}\\ &= \inf\big\{\mathcal{E}^{\mathrm{HF}}(\gamma)\,\big|\,\gamma\in\mathcal{A},\ \mathrm{Tr}[\gamma]\leq N\big\}\,.\end{aligned} \tag{26}$$

Moreover, one can write

$$\gamma^{\mathrm{HF}}(\mathbf{x},\sigma;\mathbf{y},\tau) = \sum_{i=1}^{N}\varphi_i(\mathbf{x},\sigma)\overline{\varphi_i(\mathbf{y},\tau)}\,, \tag{27}$$

with $\varphi_i\in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q), i=1,\dots,N$, orthonormal, such that the Hartree-Fock orbitals $\{\varphi_i\}_{i=1}^N$ *satisfy:*

(i) *With $h_{\gamma^{\mathrm{HF}}}$ as defined in* (25)*,*

$$h_{\gamma^{\mathrm{HF}}}\varphi_i = \varepsilon_i\varphi_i\ ,\ i=1,\dots,N\,, \tag{28}$$

with $0>\varepsilon_N\geq\ldots\geq\varepsilon_1> -\alpha^{-1}$ the N lowest eigenvalues of $h_{\gamma^{\mathrm{HF}}}$.

(ii) *For* $i = 1, \ldots, N$,

$$\varphi_i \in C^\infty(\mathbb{R}^3 \setminus \{0\}; \mathbb{C}^q)\,. \tag{29}$$

(iii) *For all* $R > 0$ *and* $\beta < \nu_{\varepsilon_N} := \sqrt{-\varepsilon_N(2\alpha^{-1} + \varepsilon_N)}$, *there exists* $C = C(R,\beta) > 0$ *such that for* $i = 1, \ldots, N$,

$$|\varphi_i(\mathbf{x})| \leq C\, e^{-\beta|\mathbf{x}|} \quad \text{for} \quad |\mathbf{x}| \geq R\,. \tag{30}$$

Remark 1.

(i) *In fact, we prove that* (29) *holds for* any *eigenfunction* φ *of* $h_{\gamma^{\mathrm{HF}}}$, *and* (30) *for those corresponding to negative eigenvalues* ε. *More precisely, if* $h_{\gamma^{\mathrm{HF}}}\varphi = \varepsilon\varphi$ *for some* $\varepsilon \in [\varepsilon_N, 0)$, *then* (30) *holds for* φ *for all* $\beta < \nu_\varepsilon := \sqrt{-\varepsilon(2\alpha^{-1} + \varepsilon)}$ *for some* $C = C(R,\beta) > 0$.

(ii) *Note that, in general, eigenfunctions of* $h_{\gamma^{\mathrm{HF}}}$ *can be unbounded at* $\mathbf{x} = 0$; *therefore* (29) *and* (30) *can only be expected to hold away from the origin.*

(iii) *Both the regularity and the exponential decay above are similar to the results in the non-relativistic case (i.e., for the operator in* (4)*; see* [13]*). However, the proof of Theorem 1 is considerably more complicated due to, on one hand, the non-locality of the kinetic energy operator* $E(\mathbf{p})$, *and, on the other hand, the fact that the Hartree-Fock operator* $h_{\gamma^{\mathrm{HF}}}$ *is only given as a* form *sum for* $Z\alpha \in [1/2, 2/\pi)$.

(iv) *We show the existence of the Hartree-Fock minimizer by solving the minimization problem on the set of density matrices. This method was introduced in* [23]. *The same method was used in* [4] *in the Dirac-Fock case.*

(v) *As mentioned earlier, we have to assume that* $Z\alpha < 2/\pi$; *the reason is that our proof that* $\mathrm{Tr}[E(\mathbf{p})\gamma_n]$ *is uniformly bounded for a minimizing sequence* $\{\gamma_n\}_{n\in\mathbb{N}}$ *does not work in the critical case* $Z\alpha = 2/\pi$.

(vi) *For simplicity of notation, we give the proof of Theorem 1 only in the spinless case. It will be obvious that the proof also works in the general case.*

(vii) *As will be clear from the proofs, the statements of Theorem 1 (appropriately modified) also hold for molecules. More explicitely, for a molecule with* K *nuclei of charges* $Z_1, \ldots, Z_K$, *fixed at* $R_1, \ldots, R_K \in \mathbb{R}^3$, *replace* $\mathfrak{v}$ *in* (6) *by*

$$\mathfrak{v}[u,v] := \sum_{k=1}^{K} (V_k^{1/2}u, V_k^{1/2}v) \quad \text{for} \quad u, v \in H^{1/2}(\mathbb{R}^3; \mathbb{C}^q)\,, \tag{31}$$

with $V_k(\mathbf{x}) = Z_k\alpha/|\mathbf{x} - R_k|, Z_k\alpha < 2/\pi$. *Then, for* $N < 1 + \sum_{k=1}^{K} Z_k$, *there exists a Hartree-Fock minimizer, and the corresponding Hartree-Fock orbitals have the regularity and decay properties as stated in Theorem 1, away from each nucleus.*

2. Proof of Theorem 1

2.1. **Existence of the Hartree-Fock minimizer.** The proof of the existence of an N-dimensional projection γ^{HF} minimizing $\mathcal{E}^{\mathrm{HF}}$, the equalities in (26), and that the corresponding Hartree-Fock orbitals $\{\varphi_i\}_{i=1}^N$ solve the Hartree-Fock equations (28), will be a consequence of the following two lemmas.

Lemma 1. *Let* $Z\alpha < 2/\pi$ *and* $N \in \mathbb{N}$. *Then*

$$E_{\leq}^{\mathrm{HF}}(N,Z,\alpha) := \inf\big\{\mathcal{E}^{\mathrm{HF}}(\gamma) \,\big|\, \gamma \in \mathcal{A}, \mathrm{Tr}[\gamma] \leq N\big\}$$

is attained.

Lemma 2. *Let $\gamma \in \mathcal{A}$. Then the operator K_γ, defined by (24), is Hilbert-Schmidt. If $Z\alpha < 2/\pi$ then the operator h_γ, defined in (25), satisfies $\sigma_{\mathrm{ess}}(h_\gamma) = [0, \infty)$. If furthermore $\mathrm{Tr}[\gamma] < Z$, then h_γ has infinitely many eigenvalues in $[-\alpha^{-1}, 0)$.*

Before proving these two lemmas, we use them to prove the parts of Theorem 1 mentioned above.

Proof. For computational reasons we first state and prove a lemma in the spirit of [3, Lemma 1].

Lemma 3. *Let $\gamma \in \mathcal{A}$, $u_1, u_2 \in H^{1/2}(\mathbb{R}^3)$, and let $\epsilon_1, \epsilon_2 \in \mathbb{R}$ be such that $\tilde\gamma$ given by*

$$\tilde\gamma(\mathbf{x},\mathbf{y}) := \gamma(\mathbf{x},\mathbf{y}) + \gamma_u(\mathbf{x},\mathbf{y}) \,, \tag{32}$$

$$\gamma_u(\mathbf{x},\mathbf{y}) := \gamma_{u_1,u_2}(\mathbf{x},\mathbf{y}) = \epsilon_1 u_1(\mathbf{x})\overline{u_1(\mathbf{y})} + \epsilon_2 u_2(\mathbf{x})\overline{u_2(\mathbf{y})} \tag{33}$$

is again an element of $\mathcal{A}$.

Then we have that

$$\mathcal{E}^{\mathrm{HF}}(\tilde\gamma) = \mathcal{E}^{\mathrm{HF}}(\gamma) + \alpha^{-1}\epsilon_1(u_1, h_\gamma u_1) + \alpha^{-1}\epsilon_2(u_2, h_\gamma u_2) + \epsilon_1\epsilon_2 R_u \,, \tag{34}$$

where h_γ is given in (25), and

$$R_u := R_{u_1,u_2} = \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{|u_1(\mathbf{x})u_2(\mathbf{y}) - u_2(\mathbf{x})u_1(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} \,. \tag{35}$$

Proof of Lemma 3: We have that

$$\begin{aligned}
\mathcal{E}^{\mathrm{HF}}(\tilde\gamma) &= \mathcal{E}^{\mathrm{HF}}(\gamma) + \alpha^{-1}\mathrm{Tr}[h_0\gamma_u] + \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_\gamma(\mathbf{x})\rho_{\gamma_u}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} \\
&\quad - \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\gamma(\mathbf{x},\mathbf{y})\overline{\gamma_u(\mathbf{x},\mathbf{y})}}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_{\gamma_u}(\mathbf{x})\rho_{\gamma_u}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} \\
&\quad - \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\gamma_u(\mathbf{x},\mathbf{y})\overline{\gamma_u(\mathbf{x},\mathbf{y})}}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} \\
&= \mathcal{E}^{\mathrm{HF}}(\gamma) + \alpha^{-1}\epsilon_1(u_1, h_\gamma u_1) + \alpha^{-1}\epsilon_2(u_2, h_\gamma u_2) \\
&\quad + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_{\gamma_u}(\mathbf{x})\rho_{\gamma_u}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} - \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\gamma_u(\mathbf{x},\mathbf{y})\overline{\gamma_u(\mathbf{x},\mathbf{y})}}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} \,.
\end{aligned} \tag{36}$$

Using (33), that $\rho_{\gamma_u}(\mathbf{x}) = \epsilon_1|u_1(\mathbf{x})|^2 + \epsilon_2|u_2(\mathbf{x})|^2$, and (35), we obtain (34). □

By Lemma 1 a minimizer $\gamma^{\mathrm{HF}} \in \mathcal{A}$, with $\mathrm{Tr}[\gamma^{\mathrm{HF}}] \le N$, exists. We may write

$$\gamma^{\mathrm{HF}}(\mathbf{x},\mathbf{y}) = \sum_k \lambda_k \varphi_k(\mathbf{x})\overline{\varphi_k(\mathbf{y})} \,, \tag{37}$$

with $1 \ge \lambda_1 \ge \cdots \ge 0$ and $\{\varphi_k\}_k \subset H^{1/2}(\mathbb{R}^3)$ an orthonormal (in $L^2(\mathbb{R}^3)$) system (it might be finite). Extend $\{\varphi_k\}_k$ to an orthonormal basis $\{\varphi_k\}_k \cup \{u_\ell\}_{\ell\in\mathbb{N}}$ for $L^2(\mathbb{R}^3)$, with $u_\ell \in H^{1/2}(\mathbb{R}^3)$.

Let $K+1$ be the first index such that $\lambda_{K+1} < 1$. Fix $j \in \{1, \ldots, K\}$, choose $u \in \{\varphi_k\}_{k\ge K+1} \cup \{u_\ell\}_{\ell\in\mathbb{N}}$, and consider, for ϵ to be chosen,

$$\gamma_\epsilon^{(j)}(\mathbf{x},\mathbf{y}) := \sum_{k\ne j} \lambda_k \varphi_k(\mathbf{x})\varphi_k^*(\mathbf{y}) + \frac{1}{1+m\epsilon^2}\big(\varphi_j(\mathbf{x}) + \epsilon u(\mathbf{x})\big)\big(\overline{\varphi_j(\mathbf{y})} + \epsilon\overline{u(\mathbf{y})}\,\big) \,.$$

Choosing $m \ge 1$ assures that $\mathrm{Tr}[\gamma_\epsilon^{(j)}] \le N$. Then $0 \le \gamma_\epsilon^{(j)} \le \mathrm{Id}$ for $|\epsilon|$ small enough (depending on u). Since γ^{HF} minimizes $\mathcal{E}^{\mathrm{HF}}$, and $\gamma_0^{(j)} = \gamma^{\mathrm{HF}}$,

$$0 = \frac{d}{d\epsilon}(\mathcal{E}^{\mathrm{HF}})\big(\gamma_\epsilon^{(j)}\big)\Big|_{\epsilon=0} = \alpha^{-1}(\varphi_j, h_{\gamma^{\mathrm{HF}}}u) + \alpha^{-1}(u, h_{\gamma^{\mathrm{HF}}}\varphi_j) \,.$$

Repeating the computation for iu we get that $(u, h_{\gamma^{\rm HF}}\varphi_j) = 0$, from which it follows that $h_{\gamma^{\rm HF}}$ maps $\mathrm{span}\{\varphi_1, \dots, \varphi_K\}$ into itself. Diagonalising the restriction of $h_{\gamma^{\rm HF}}$ to $\mathrm{span}\{\varphi_1, \dots, \varphi_K\}$, we can choose $\varphi_1, \dots, \varphi_K$ to be eigenfunctions of $h_{\gamma^{\rm HF}}$ with eigenvalues $\varepsilon_{n_1}, \dots, \varepsilon_{n_K}$, $n_j \in \mathbb{N}$ (numbering the eigenvalues of $h_{\gamma^{\rm HF}}$ in increasing order, $-\alpha^{-1} < \varepsilon_1 \le \varepsilon_2 \le \cdots$). Since $\lambda_1 = \cdots = \lambda_K = 1$, this does not change (37).

To show that, for $j > K$, φ_j is also an eigenfunction of $h_{\gamma^{\rm HF}}$ (corresponding to an eigenvalue ε_{n_j}) one repeats the argument above, with $u \in \{\varphi_k\}_{k\neq 1,\dots,K,j} \cup \{u_\ell\}_{\ell\in\mathbb{N}}$, and

$$\gamma_\epsilon^{(j)}(\mathbf{x},\mathbf{y}) = \sum_{k\neq j} \lambda_k \varphi_k(\mathbf{x})\overline{\varphi_k(\mathbf{y})} + \frac{\lambda_j}{1+m\epsilon^2}\big(\varphi_j(\mathbf{x}) + \epsilon u(\mathbf{x})\big)\big(\,\overline{\varphi_j(\mathbf{y})} + \epsilon\overline{u(\mathbf{y})}\,\big)\,.$$

Moreover, the eigenvalues ε_{n_k} (of $h_{\gamma^{\rm HF}}$) corresponding to the eigenfunctions φ_k are non-positive. In fact, if $\varepsilon_{n_k} > 0$, then we could lower the energy: Define $\tilde\gamma(\mathbf{x},\mathbf{y}) = \gamma^{\rm HF}(\mathbf{x},\mathbf{y}) - \lambda_k\varphi_k(\mathbf{x})\overline{\varphi_k(\mathbf{y})}$, then, using Lemma 3, we get that $\mathcal{E}^{\rm HF}(\tilde\gamma) = \mathcal{E}^{\rm HF}(\gamma^{\rm HF}) - \alpha^{-1}\lambda_k\varepsilon_{n_k} < \mathcal{E}^{\rm HF}(\gamma^{\rm HF})$.

It remains to show that $\mathrm{Tr}[\gamma^{\rm HF}] = N$, that $\gamma^{\rm HF}$ is a projection, and that the $\{\varphi_j\}_{j=1}^N$ are eigenfunctions corresponding to the *lowest* (negative) eigenvalues of $h_{\gamma^{\rm HF}}$ (that is, to $\varepsilon_1 \le \varepsilon_2 \le \cdots \le \varepsilon_N < 0$).

Consider first the case $N < Z$. Assume, for contradiction, that $\mathrm{Tr}[\gamma^{\rm HF}] < N$. Let $K \in \mathbb{N}$ be the multiplicity of the eigenvalue 1 in (37). Since (by Lemma 2), for $N < Z$, $h_{\gamma^{\rm HF}}$ has infinitely many eigenvalues in $[-\alpha^{-1}, 0)$ we can find a (normalized) eigenfunction u, corresponding to a negative eigenvalue of $h_{\gamma^{\rm HF}}$, and orthogonal to $\varphi_1, \dots, \varphi_K$. Let $\epsilon > 0$ be sufficiently small that $\gamma(\mathbf{x},\mathbf{y}) := \gamma^{\rm HF}(\mathbf{x},\mathbf{y}) + \epsilon u(\mathbf{x})\overline{u(\mathbf{y})}$ defines a density matrix satisfying $\mathrm{Tr}[\gamma] \le N$. By Lemma 3 (with $u_1 = u, \epsilon_1 = \epsilon$ and $\epsilon_2 = 0$) we get that

$$\mathcal{E}^{\rm HF}(\gamma) = \mathcal{E}^{\rm HF}(\gamma^{\rm HF}) + \epsilon\alpha^{-1}(u, h_{\gamma^{\rm HF}}u) < \mathcal{E}^{\rm HF}(\gamma^{\rm HF})\,, \tag{38}$$

leading to a contradiction. Hence, $\mathrm{Tr}[\gamma^{\rm HF}] = N$. That $\gamma^{\rm HF}$ is a projection follows from Lieb's Variational Principle (see [11]) which we prove for completeness. If this is not the case, there exist indices p, q such that $0 < \lambda_p, \lambda_q < 1$. Consider $\tilde\gamma(\mathbf{x},\mathbf{y}) := \gamma^{\rm HF}(\mathbf{x},\mathbf{y}) + \epsilon\varphi_q(\mathbf{x})\overline{\varphi_q(\mathbf{y})} - \epsilon\varphi_p(\mathbf{x})\overline{\varphi_p(\mathbf{y})}$ with ϵ such that $0 \le \tilde\gamma \le \mathrm{Id}$. Choose $\epsilon > 0$ if $\varepsilon_{n_q} \le \varepsilon_{n_p}$ and $\epsilon < 0$ otherwise. By Lemma 3, we get that $\mathcal{E}^{\rm HF}(\tilde\gamma) < \mathcal{E}^{\rm HF}(\gamma^{\rm HF})$.

Consider now the case $Z \le N < Z+1$ (and $N \ge 2$), so that $N - 1 < Z$. Let $\gamma_{N-1}^{\rm HF}$ denote the density matrix where

$$\inf\big\{\mathcal{E}^{\rm HF}(\gamma)\,\big|\,\gamma \in \mathcal{A},\ \mathrm{Tr}[\gamma] \le N-1\big\}$$

is attained. By the above, $\mathrm{Tr}[\gamma_{N-1}^{\rm HF}] = N-1$ and $\gamma_{N-1}^{\rm HF}$ is a projection, so its integral kernel is given by

$$\gamma_{N-1}^{\rm HF}(\mathbf{x},\mathbf{y}) = \sum_{i=1}^{N-1} \phi_i(\mathbf{x})\overline{\phi_i(\mathbf{y})}\,,$$

where the ϕ_i's are eigenfunctions of $h_{\gamma_{N-1}^{\rm HF}}$.

We first prove that

$$\inf\big\{\mathcal{E}^{\rm HF}(\gamma)\,\big|\,\gamma \in \mathcal{A},\ \mathrm{Tr}[\gamma] \le N\big\} \tag{39}$$

is not attained at the density matrix $\gamma_{N-1}^{\rm HF}$ by constructing a density matrix $\tilde\gamma$ with $\mathrm{Tr}[\tilde\gamma] \le N$ such that $\mathcal{E}^{\rm HF}(\tilde\gamma) < \mathcal{E}^{\rm HF}(\gamma_{N-1}^{\rm HF})$. Indeed, since $h_{\gamma_{N-1}^{\rm HF}}$ has infinitely many strictly negative eigenvalues (by Lemma 2; $N-1 < Z$) there exists a (normalized) eigenfunction u of $h_{\gamma_{N-1}^{\rm HF}}$ corresponding to a negative eigenvalue, and orthogonal to

$\mathrm{span}\{\phi_1,\ldots,\phi_{N-1}\}$. Let $\tilde\gamma$ be defined by

$$\tilde\gamma(\mathbf{x},\mathbf{y}) = \gamma^{\mathrm{HF}}_{N-1}(\mathbf{x},\mathbf{y}) + u(\mathbf{x})\overline{u(\mathbf{y})}\,.$$

Then $\mathrm{Tr}[\tilde\gamma]=N$ and, by a computation like in (38),

$$\mathcal{E}^{\mathrm{HF}}(\tilde\gamma) = \mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}_{N-1}) + \alpha^{-1}(u, h_{\gamma^{\mathrm{HF}}_{N-1}}u) < \mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}_{N-1})\,.$$

Hence,

$$\inf\left\{\mathcal{E}^{\mathrm{HF}}(\gamma)\,\middle|\,\gamma\in\mathcal{A}, \mathrm{Tr}[\gamma]\le N\right\} < \inf\left\{\mathcal{E}^{\mathrm{HF}}(\gamma)\,\middle|\,\gamma\in\mathcal{A}, \mathrm{Tr}[\gamma]\le N-1\right\}. \qquad (40)$$

Let γ_N be a density matrix where (39) is attained (the existence of such a minimizer follows, as before, from Lemma 1). By the above it follows that $N-1 < \mathrm{Tr}[\gamma_N]\le N$. We now show that there exists a minimizer γ^{HF} with $\mathrm{Tr}[\gamma^{\mathrm{HF}}]=N$.

The integral kernel of γ_N is given by

$$\gamma_N(\mathbf{x},\mathbf{y}) = \sum_j \lambda_j\varphi_j(\mathbf{x})\overline{\varphi_j(\mathbf{y})}\,,$$

where $1\ge\lambda_1\ge\cdots\ge 0$ and the φ_j's are (orthonormal) eigenfunctions of h_{γ_N}. If $\mathrm{Tr}[\gamma_N]<N$ we can define a new density matrix $\tilde\gamma$ with $\mathrm{Tr}[\tilde\gamma]\le N$ and $\mathcal{E}^{\mathrm{HF}}(\tilde\gamma)\le \mathcal{E}^{\mathrm{HF}}(\gamma_N)$. Indeed, if $\mathrm{Tr}[\gamma_N]<N$ (and bigger than $N-1$) then there exists a (first) j_0 such that $0<\lambda_{j_0}<1$. We define $\tilde\gamma$ with integral kernel

$$\tilde\gamma(\mathbf{x},\mathbf{y}) = \gamma_N(\mathbf{x},\mathbf{y}) + r\varphi_{j_0}(\mathbf{x})\overline{\varphi_{j_0}(\mathbf{y})}\,, \qquad (41)$$

with $r=\min\{1-\lambda_{j_0}, N-\mathrm{Tr}[\gamma_N]\}>0$. Recall that $h_{\gamma_N}\varphi_j=\varepsilon_{n_j}\varphi_j$, $\varepsilon_{n_j}\le 0$, for all j. By Lemma 3 we have that

$$\mathcal{E}^{\mathrm{HF}}(\tilde\gamma) = \mathcal{E}^{\mathrm{HF}}(\gamma_N) + \alpha^{-1}r\varepsilon_{n_{j_0}}\,.$$

If $\varepsilon_{n_{j_0}}<0$, it follows that $\mathcal{E}^{\mathrm{HF}}(\tilde\gamma)<\mathcal{E}^{\mathrm{HF}}(\gamma_N)$. On the other hand, if $\varepsilon_{n_{j_0}}=0$, then $\mathcal{E}^{\mathrm{HF}}(\tilde\gamma)=\mathcal{E}^{\mathrm{HF}}(\gamma_N)$, and $\mathrm{Tr}[\gamma_N]<\mathrm{Tr}[\tilde\gamma]\le N$. Either $\mathrm{Tr}[\tilde\gamma]=N$, in which case we let $\gamma^{\mathrm{HF}}:=\tilde\gamma$, and, as above, we are done. Or, we repeat all of the above argument on

$$\tilde\gamma(\mathbf{x},\mathbf{y}) = \sum_{j=1}^{j_0}\varphi_j(\mathbf{x})\overline{\varphi_j(\mathbf{y})} + \sum_{j>j_0}\lambda_j\varphi_j(\mathbf{x})\overline{\varphi_j(\mathbf{y})}\,.$$

Since the trace stays bounded by N, this procedure has to stop eventually. Hence, with γ^{HF} the resulting density matrix, $\mathrm{Tr}[\gamma^{\mathrm{HF}}]=N$ and by Lieb's Variational Principle it follows (as above) that γ^{HF} is a projection.

Finally, let $\{\varphi_j\}$ be the eigenfunctions of $h_{\gamma^{\mathrm{HF}}}$, now numbered corresponding to the eigenvalues $\varepsilon_1\le\varepsilon_2\le\cdots$, where ε_1 is the lowest eigenvalue of $h_{\gamma^{\mathrm{HF}}}$. We know that, for some $j_1,\ldots,j_N\in\mathbb{N}$,

$$\gamma^{\mathrm{HF}}(\mathbf{x},\mathbf{y}) = \sum_{k=1}^{N}\varphi_{j_k}(\mathbf{x})\overline{\varphi_{j_k}(\mathbf{y})}\,.$$

Suppose for contradiction that $\{\varepsilon_{j_1},\ldots,\varepsilon_{j_N}\}\ne\{\varepsilon_1,\ldots,\varepsilon_N\}$. Then there exists a $k\in\{1,\ldots,N\}$ with $\varepsilon_{j_k}>\varepsilon_k$. For $\delta\in(0,1)$ define

$$\tilde\gamma(\mathbf{x},\mathbf{y}) = \gamma^{\mathrm{HF}}(\mathbf{x},\mathbf{y}) + \delta\varphi_k(\mathbf{x})\overline{\varphi_k(\mathbf{y})} - \delta\varphi_{j_k}(\mathbf{x})\overline{\varphi_{j_k}(\mathbf{y})}\,.$$

By Lemma 3,

$$\mathcal{E}^{\mathrm{HF}}(\tilde\gamma) = \mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) + \delta\alpha^{-1}(\varepsilon_k-\varepsilon_{j_k}) - \delta^2R_{\varphi_j,\varphi_{j_k}} < \mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}})\,,$$

where the last inequality follows by choosing δ small enough.

It remains to prove that $\varepsilon_1, \dots, \varepsilon_N$ are strictly negative. For $N < Z$ this follows directly from Lemma 2. In the case $Z \le N < Z+1$, assume, for contradiction, that $\varepsilon_N = 0$; then the density matrix

$$\tilde\gamma(\mathbf{x},\mathbf{y}) := \gamma^{\rm HF}(\mathbf{x},\mathbf{y}) - \varphi_N(\mathbf{x})\overline{\varphi_N(\mathbf{y})}$$

satisfies $\mathcal{E}^{\rm HF}(\tilde\gamma) = \mathcal{E}^{\rm HF}(\gamma^{\rm HF})$ (by Lemma 3) and $\mathrm{Tr}[\tilde\gamma] = N-1$. This is a contradiction to (40).

This finishes the proof of the first part of Theorem 1. □

It remains to prove Lemma 1 and Lemma 2.

Proof of Lemma 1: We minimize on density matrices following the method in [23]. In the pseudorelativistic context one faces the problem that the Coulomb potential is not relatively compact with respect to the kinetic energy. This problem has been adressed in [4] and we follow the idea therein.

The quantity $E^{\rm HF}_{\le}(N,Z,\alpha)$ is finite since for any density matrix γ, with $\mathrm{Tr}[\gamma] \le N$,

$$\mathcal{E}^{\rm HF}(\gamma) \ge \alpha^{-1}\big\{\,\mathrm{Tr}[E(\mathbf{p})\gamma] - \alpha^{-1}N - \mathrm{Tr}[V\gamma]\big\} \ge \,-\,\alpha^{-2}N\,.$$

Here we used that $\mathcal{D}(\gamma) - \mathcal{E}x(\gamma) \ge 0$, and (8) (see also (17) and (18)).

Let $\{\gamma_n\}_{n=1}^\infty$ be a minimizing sequence for $E^{\rm HF}_{\le}(N,Z,\alpha)$, more precisely, $\gamma_n \in \mathcal{A}$ (with $\mathcal{A}$ as defined in (16)), $\mathrm{Tr}[\gamma_n] \le N$, and $\mathcal{E}^{\rm HF}(\gamma_n) \le E^{\rm HF}_{\le}(N,Z,\alpha) + 1/n$.

The sequence $\mathrm{Tr}[E(\mathbf{p})\gamma_n]$ is uniformly bounded. Indeed, for every $n \in \mathbb{N}$, using (8),

$$\begin{aligned} E^{\rm HF}(N,Z,\alpha) + 1 \ge \mathcal{E}^{\rm HF}(\gamma_n) &\ge \alpha^{-1}\big\{\,\mathrm{Tr}[E(\mathbf{p})\gamma_n] - \alpha^{-1}N - \mathrm{Tr}[V\gamma_n]\big\} \\ &\ge \alpha^{-1}(1 - Z\alpha\frac{\pi}{2})\,\mathrm{Tr}[E(\mathbf{p})\gamma_n] - \alpha^{-2}N\,. \end{aligned}$$

The claim follows since $Z\alpha < 2/\pi$. It is this argument that prevents us from proving Theorem 1 for the critical case $Z\alpha = 2/\pi$.

Define $\tilde\gamma_n := E(\mathbf{p})^{1/2}\gamma_n E(\mathbf{p})^{1/2}$. Then, by the above, $\{\tilde\gamma_n\}_{n\in\mathbb{N}}$ is a sequence of Hilbert-Schmidt operators with uniformly bounded Hilbert-Schmidt norm. Hence, by Banach-Alaoglu's theorem, there exist a subsequence, which we denote again by $\tilde\gamma_n$, and a Hilbert-Schmidt operator $\tilde\gamma_{(\infty)}$, such that for every Hilbert-Schmidt operator W,

$$\mathrm{Tr}[W\tilde\gamma_n] \to \mathrm{Tr}[W\tilde\gamma_{(\infty)}]\ ,\ n\to\infty\,.$$

Let $\gamma_{(\infty)} := E(\mathbf{p})^{-1/2}\tilde\gamma_{(\infty)}E(\mathbf{p})^{-1/2}$. We are going to show that $\gamma_{(\infty)}$ is a minimizer of $\mathcal{E}^{\rm HF}$ (in fact, of $\alpha\mathcal{E}^{\rm HF}$, which is equivalent). We first prove that $\gamma_{(\infty)} \in \mathcal{A}$, then that $\mathcal{E}^{\rm HF}$ is weak lower semicontinuous on $\mathcal{A}$.

Let $\{\psi_k\}_{k\in\mathbb{N}}$ be a basis of $L^2(\mathbb{R}^3)$ with $\psi_k \in H^{1/2}(\mathbb{R}^3)$. Then, for all $k \in \mathbb{N}$,

$$\begin{aligned} \lim_{n\to\infty}(\psi_k, \gamma_n\psi_k) &= \lim_{n\to\infty}(\psi_k, E(\mathbf{p})^{-1/2}\tilde\gamma_n E(\mathbf{p})^{-1/2}\psi_k) \\ &= (\psi_k, \gamma_{(\infty)}\psi_k)\,. \end{aligned}$$

From this follows, by Fatou's lemma, that

$$\mathrm{Tr}[\gamma_{(\infty)}] = \sum_k(\psi_k,\gamma_{(\infty)}\psi_k) \le \liminf_{n\to\infty}\sum_k(\psi_k,\gamma_n\psi_k) = \liminf_{n\to\infty}\mathrm{Tr}[\gamma_n] \le N\,,$$

and

$$\mathrm{Tr}[E(\mathbf{p})^{1/2}\gamma_{(\infty)}E(\mathbf{p})^{1/2}] \le \liminf_{n\to\infty}\mathrm{Tr}[E(\mathbf{p})^{1/2}\gamma_n E(\mathbf{p})^{1/2}] < \infty\,.$$

Since also $0 \le \gamma_{(\infty)} \le \mathrm{Id}$ we see that $\gamma_{(\infty)} \in \mathcal{A}$.

To reach the claim it remains to show the weak lower semicontinuity of the functional $\mathcal{E}^{\rm HF}$. As mentioned in the introduction, the spectrum of the one-particle operator h_0, defined in (9), is discrete in $[-\alpha^{-1}, 0)$ and purely absolutely continuous in $[0, \infty)$. Let $\Lambda_-(\alpha)$ denote the projection on the pure point spectrum of h_0 and $\Lambda_+(\alpha) := \mathrm{Id} - \Lambda_-(\alpha)$. We write

$$\alpha \mathcal{E}^{\mathrm{HF}}(\gamma_n) = T_1(\gamma_n) + T_2(\gamma_n) + \alpha T_3(\gamma_n)\,, \tag{42}$$

with

$$T_1(\gamma_n) = \mathrm{Tr}[\Lambda_+(\alpha) h_0 \Lambda_+(\alpha)\gamma_n]\ , \quad T_2(\gamma_n) = \mathrm{Tr}[\Lambda_-(\alpha) h_0 \Lambda_-(\alpha)\gamma_n]\,,$$
$$T_3(\gamma_n) = \mathcal{D}(\gamma_n) - \mathcal{E}x(\gamma_n)\,.$$

We consider these three terms separately.

For the first term in (42), fix (as above) a basis $\{\psi_k\}_{k\in\mathbb{N}}$ of $L^2(\mathbb{R}^3)$, with $\{\psi_k\}_{k\in\mathbb{N}} \subset H^{1/2}(\mathbb{R}^3)$. Defining

$$f_k := \big(\Lambda_+(\alpha) h_0 \Lambda_+(\alpha)\big)^{1/2}\psi_k\,,$$

we have that

$$\begin{aligned} T_1(\gamma_n) &= \mathrm{Tr}\left[\big(\Lambda_+(\alpha) h_0 \Lambda_+(\alpha)\big)^{1/2}\gamma_n\big(\Lambda_+(\alpha) h_0 \Lambda_+(\alpha)\big)^{1/2}\right] \\ &= \sum_k (f_k, \gamma_n f_k) = \sum_k (E(\mathbf{p})^{-1/2} f_k, \tilde{\gamma}_n E(\mathbf{p})^{-1/2} f_k)\,. \end{aligned}$$

Since the projection

$$H_k := \big|E(\mathbf{p})^{-1/2} f_k\big\rangle \big\langle E(\mathbf{p})^{-1/2} f_k\big|$$

is a non-negative Hilbert-Schmidt operator, we find, by Fatou's lemma, that

$$\liminf_{n\to\infty} T_1(\gamma_n) = \liminf_{n\to\infty} \sum_k \mathrm{Tr}[H_k \tilde{\gamma}_n] \geq \sum_k \mathrm{Tr}[H_k \tilde{\gamma}_{(\infty)}] = T_1(\gamma_{(\infty)})\,.$$

As for the second term in (42), we have $\lim_{n\to\infty} T_2(\gamma_n) = T_2(\gamma_{(\infty)})$ since the operator $\Lambda_-(\alpha) h_0 \Lambda_-(\alpha)$ is Hilbert-Schmidt; see Lemma 7 in Appendix A.

Finally, for the last term in (42), following the reasoning in [4, pp.142–143] (here we need that $N \in \mathbb{N}$), we get that

$$\liminf_{n\to\infty} T_3(\gamma_n) \geq T_3(\gamma_{(\infty)})\,.$$

This finishes the proof of Lemma 1. □

Proof of Lemma 2: In order to prove that K_γ is Hilbert-Schmidt it is enough to prove that its integral kernel belongs to $L^2(\mathbb{R}^6)$. We have that (see (24) and (14))

$$\begin{aligned} \int_{\mathbb{R}^6} |K_\gamma(\mathbf{x},\mathbf{y})|^2\, d\mathbf{x} d\mathbf{y} &= \int_{\mathbb{R}^6} \frac{|\gamma(\mathbf{x},\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|^2}\, d\mathbf{x} d\mathbf{y} \\ &= \sum_{j,k} \lambda_j \lambda_k \int_{\mathbb{R}^6} \frac{\overline{u_k(\mathbf{x})} u_j(\mathbf{x}) u_k(\mathbf{y}) \overline{u_j(\mathbf{y})}}{|\mathbf{x}-\mathbf{y}|^2}\, d\mathbf{x} d\mathbf{y} =: \sum_{j,k} \lambda_j \lambda_k I_{j,k}\,. \end{aligned} \tag{43}$$

The last integral can be estimated using the Hardy-Littlewood-Sobolev, Hölder, and Sobolev inequalities (in that order), to get

$$I_{j,k} \leq \|u_k u_j\|_{3/2}^2 \leq \|u_k\|_3^2 \|u_j\|_3^2 \leq C \|u_k\|_{H^{1/2}}^2 \|u_j\|_{H^{1/2}}^2\,. \tag{44}$$

Inserting (44) in (43) we obtain (since $\gamma \in \mathcal{A}$)

$$\begin{aligned} \int_{\mathbb{R}^6} |K_\gamma(\mathbf{x},\mathbf{y})|^2\, d\mathbf{x} d\mathbf{y} &\leq C \sum_{j,k} \lambda_j \lambda_k \|u_k\|_{H^{1/2}}^2 \|u_j\|_{H^{1/2}}^2 = C\Big(\sum_j \lambda_j \|u_j\|_{H^{1/2}}^2\Big)^2 \\ &= C\big(\mathrm{Tr}[E(\mathbf{p})\gamma]\big)^2 < \infty\,. \end{aligned}$$

To prove the statement on the essential spectrum, define $\tilde{h}_\gamma := h_\gamma + \alpha K_\gamma$. Since K_γ is Hilbert-Schmidt, and $\sigma_{\mathrm{ess}}(h_0) = [0, \infty)$ (see the introduction), it is enough to prove that $(\tilde{h}_\gamma+\eta)^{-1}-(h_0+\eta)^{-1}$ is compact for some $\eta>0$ large enough [20, Theorem XIII.14]. Since $\mathcal{D}(h_0)=\mathcal{D}(\tilde{h}_\gamma)\subset\mathcal{D}(R_\gamma)$, we have that

$$(\tilde{h}_\gamma+\eta)^{-1}-(h_0+\eta)^{-1} = -(\tilde{h}_\gamma+\eta)^{-1}\alpha R_\gamma(h_0+\eta)^{-1}\,. \tag{45}$$

From Tiktopoulos's formula (see [22, (II.8), Section II.3]), it follows that

$$\begin{aligned}&(h_0+\eta)^{-1}\\ &\quad=(T(\mathbf{p})+\eta)^{-1/2}[1-(T(\mathbf{p})+\eta)^{-1/2}V(T(\mathbf{p})+\eta)^{-1/2}]^{-1}(T(\mathbf{p})+\eta)^{-1/2}\,.\end{aligned} \tag{46}$$

Since, by (5), $\|(T(\mathbf{p})+\eta)^{-1/2}V^{1/2}\|<1$ for $Z\alpha<2/\pi$ and $\eta>\alpha^{-1}$, the right side of (46) is well defined. Inserting (46) in (45) one sees that it suffices to prove that $R_\gamma(T(\mathbf{p})+\eta)^{-1/2}$ is compact. That this is indeed the case follows by using [19, Theorem XI.20] together with the observation that, for $\varepsilon>0$ and $\eta>\alpha^{-1}$, R_γ and $(T(\mathbf{p})+\eta)^{-1/2}$ (as a function of $\mathbf{p}$) belong to the space $L^{6+\varepsilon}(\mathbb{R}^3)$ (for R_γ, see (23)).

Finally, we show that if $\mathrm{Tr}[\gamma]=N<Z$ then h_γ has infinitely many eigenvalues in $[-\alpha^{-1},0)$. By the min-max principle [20, Theorem XIII.1] and since $\sigma_{\mathrm{ess}}(h_\gamma)=[0,\infty)$, it is sufficient to show that for every $n\in\mathbb{N}$ we can find n orthogonal functions $u_1,\dots,u_n$ in $L^2(\mathbb{R}^3)$ such that $(u_i,h_\gamma u_i)<0$ for $i=1,\dots,n$.

Let $n\in\mathbb{N}$. Fix $\delta:=1-N/Z$ and let $h_{0,\delta}$ be the unique self-adjoint operator whose quadratic form domain is $H^{1/2}(\mathbb{R}^3)$ such that

$$(u,h_{0,\delta}v)=\mathfrak{t}[u,v]-\delta\,\mathfrak{v}[u,v]\ \text{for}\ u,v\in H^{1/2}(\mathbb{R}^3)\,.$$

By [7, Theorems 2.2 and 2.3], $\sigma_{\mathrm{ess}}(h_{0,\delta})=[0,\infty)$. Moreover, $h_{0,\delta}$ has infinitely many eigenvalues in $[-\alpha^{-1},0)$. This follows by the min-max principle and the inequality $h_{0,\delta}\le\alpha/2(-\Delta)-\delta Z\alpha/|\mathbf{x}|$. Hence, we can find $u_1,\dots,u_n$ spherically symmetric and orthonormal such that $(u_i,h_{0,\delta}u_i)<0$ for $i=1,\dots,n$. Then, by the positivity of K_γ, by Newton's Theorem [12, p. 249], and since $\mathrm{Tr}[\gamma]=N$ we get, for $i=1,\dots,n$, that

$$\begin{aligned}(u_i,h_\gamma u_i)&\le\mathfrak{t}[u_i,u_i]-\mathfrak{v}[u_i,u_i]+\alpha(u_i,R_\gamma u_i)\\&\le\mathfrak{t}[u_i,u_i]-\mathfrak{v}[u_i,u_i]+\frac{N}{Z}\mathfrak{v}[u_i,u_i]=(u_i,h_{0,\delta}u_i)<0\,.\end{aligned}$$

The claim follows. □

2.2. **Regularity of the Hartree-Fock orbitals.** Here we prove that any eigenfunction of $h_{\gamma^{\mathrm{HF}}}$ is in $C^\infty(\mathbb{R}^3\setminus\{0\})$.

Proof. Let φ be a solution of $h_{\gamma^{\mathrm{HF}}}\varphi=\varepsilon\varphi$ for some $\varepsilon\in\mathbb{R}$. Then φ belongs to the domain of the operator and in particular to $H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)$. We are going to prove that $\varphi\in H^k(\Omega)$ for all bounded smooth $\Omega\subset\mathbb{R}^3\setminus\{0\}$ and all $k\in\mathbb{N}$. The claim will then follow from the Sobolev imbedding theorem [2, Theorem 4.12]. We will use results on pseudodifferential operators; see Appendix B. We briefly summarize these here.

1) For all $k,\ell\in\mathbb{R}$, $E(\mathbf{p})^\ell$ maps $H^k(\mathbb{R}^3)$ to $H^{k-\ell}(\mathbb{R}^3)$.
2) For all $k,\ell\in\mathbb{R}$, and any $\chi\in C_0^\infty(\mathbb{R}^3)$, the commutator $[\chi,E(\mathbf{p})^\ell]$ maps $H^k(\mathbb{R}^3)$ to $H^{k-\ell+1}(\mathbb{R}^3)$.
3) For all $k,\ell,m\in\mathbb{R}$ and $\chi_1,\chi_2\in C_0^\infty(\mathbb{R})$ with $\operatorname{supp}\chi_1\cap\operatorname{supp}\chi_2=\emptyset$, $\chi_1E(\mathbf{p})^\ell\chi_2$ maps $H^k(\mathbb{R}^3)$ to $H^m(\mathbb{R}^3)$. Such an operator is called 'smoothing'.

Fix Ω a bounded smooth subset of $\mathbb{R}^3\setminus\{0\}$. We proceed by induction on $k\in\mathbb{N}$. Assume that $\varphi\in H^k(\Omega)$ for some $k\ge0$, i.e., $\chi\varphi\in H^k(\mathbb{R}^3)$ for all $\chi\in C_0^\infty(\Omega)$. Notice that $H^k(\mathbb{R}^3)=D(E(\mathbf{p})^k)$.

Since $\chi\varphi \in H^{k+1}(\mathbb{R}^3)$ is equivalent to $\chi\varphi \in D(E(\mathbf{p})^{k+1})$, and $D(E(\mathbf{p})^{k+1}) = D((E(\mathbf{p})^{k+1})^*)$, it is sufficient to prove that $\chi\varphi \in D((E(\mathbf{p})^{k+1})^*)$, or equivalently, that there exists $v \in L^2(\mathbb{R}^3)$ such that

$$(\chi\varphi, E(\mathbf{p})^{k+1} f) = (v, f) \quad \text{for all } f \in H^{k+1}(\mathbb{R}^3)\,.$$

Let $f \in H^{k+1}(\mathbb{R}^3)$. Then

$$\begin{aligned}(\chi\varphi, E(\mathbf{p})^{k+1} f) &= \mathfrak{e}(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) \\ &= (\varepsilon + \alpha^{-1})(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) + \mathfrak{v}(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) \\ &\quad - \mathfrak{b}_{\gamma^{\mathrm{HF}}}(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f)\,, \end{aligned} \tag{47}$$

where we use that $h_{\gamma^{\mathrm{HF}}}\varphi = \varepsilon\varphi$. We study the terms in (47) separately. In the following, $\tilde{\chi}$ denotes a function in $C_0^\infty(\Omega)$ with $\tilde{\chi} \equiv 1$ on $\operatorname{supp}\chi$.

For the first term in (47) we find that

$$\begin{aligned}&(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) = (\chi E(\mathbf{p})^{-1}\varphi, E(\mathbf{p})^{k+1} f) \\ &= ([\chi, E(\mathbf{p})^{-1}]\varphi, E(\mathbf{p})^{k+1} f) + (E(\mathbf{p})^{-1}\chi\varphi, E(\mathbf{p})^{k+1} f)\,. \end{aligned} \tag{48}$$

Since $\chi\varphi \in H^k(\mathbb{R}^3)$ by the induction hypothesis, we have that $E(\mathbf{p})^{-1}\chi\varphi \in H^{k+1}(\mathbb{R}^3)$ and hence there exists $w_1 \in L^2(\mathbb{R}^3)$ such that

$$(E(\mathbf{p})^{-1}\chi\varphi, E(\mathbf{p})^{k+1} f) = (w_1, f)\,.$$

It remains to study the first term in (48). We have that

$$\begin{aligned}&([\chi, E(\mathbf{p})^{-1}]\varphi, E(\mathbf{p})^{k+1} f) \\ &= ([\chi, E(\mathbf{p})^{-1}]\tilde{\chi}\varphi, E(\mathbf{p})^{k+1} f) + ([\chi, E(\mathbf{p})^{-1}](1-\tilde{\chi})\varphi, E(\mathbf{p})^{k+1} f)\,.\end{aligned}$$

Since $\tilde{\chi}\varphi \in H^k(\mathbb{R}^3)$ by the induction hypothesis, it follows from Proposition 2 that $[\chi, E(\mathbf{p})^{-1}]\tilde{\chi}\varphi$ belongs to $H^{k+2}(\mathbb{R}^3)$. On the other hand since the supports of χ and $\tilde{\chi}$ are disjoint the operator $[\chi, E(\mathbf{p})^{-1}](1-\tilde{\chi})$ is a smoothing operator. Hence there exists a $w_2 \in L^2(\mathbb{R}^3)$ such that

$$([\chi, E(\mathbf{p})^{-1}]\varphi, E(\mathbf{p})^{k+1} f) = (w_2, f)\,.$$

As for the second term in (47), we find, with $\tilde{\chi}$ as before,

$$\begin{aligned}\mathfrak{v}(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) &= (\varphi, VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) \\ &= (\tilde{\chi}\varphi, VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) \\ &\quad + ((1-\tilde{\chi})\varphi, VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f)\,.\end{aligned} \tag{49}$$

Since $\tilde{\chi}$ has support away from zero, $V\tilde{\chi}\varphi \in H^k(\mathbb{R}^3)$ and hence there exists $w_3 \in L^2(\mathbb{R}^3)$ such that

$$(\tilde{\chi}\varphi, VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) = (w_3, f)\,.$$

For the second term in (49) we proceed via an approximation. Let $\{\varphi_n\}_{n=1}^\infty \subset C_0^\infty(\mathbb{R}^3)$ such that $\varphi_n \to \varphi, n \to \infty$, in $L^2(\mathbb{R}^3)$. Since $(1-\tilde{\chi})VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f$ belongs to $L^2(\mathbb{R}^3)$, we have that

$$(\varphi, (1-\tilde{\chi})VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) = \lim_{n\to+\infty}(\varphi_n, (1-\tilde{\chi})VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f)\,.$$

For each $n \in \mathbb{N}$, $V(1-\tilde{\chi})\varphi_n \in H^m(\mathbb{R}^3)$ for all m, since $\varphi_n \in C_0^\infty(\mathbb{R}^3)$, and V maps $H^k(\mathbb{R}^3)$ into $H^{k-1}(\mathbb{R}^3)$ for all k. Therefore, $E(\mathbf{p})^{k+1}\chi E(\mathbf{p})^{-1}V(1-\tilde{\chi})\varphi_n \in L^2(\mathbb{R}^3)$, and so

$$\begin{aligned}&(\varphi_n, (1-\tilde{\chi})VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) \\ &= (E(\mathbf{p})^{k+1}\chi E(\mathbf{p})^{-1}V(1-\tilde{\chi})\varphi_n, f) \\ &= (E(\mathbf{p})^{k+1}\chi E(\mathbf{p})^{-1}(1-\tilde{\chi})E(\mathbf{p})E(\mathbf{p})^{-1}V\varphi_n, f)\,.\end{aligned}$$

Here $E(\mathbf{p})^{-1}V$ is bounded by (8), and $\chi E(\mathbf{p})^{-1}(1-\tilde{\chi})$ is a smoothing operator by the choice of the supports of χ and $\tilde{\chi}$. It then follows that $\{E(\mathbf{p})^{k+1}\chi E(\mathbf{p})^{-1}(1-\tilde{\chi})E(\mathbf{p})E(\mathbf{p})^{-1}V\varphi_n\}_{n\in\mathbb{N}}$ is a uniformly bounded sequence in $L^2(\mathbb{R}^3)$ and hence there exists $w_4 \in L^2(\mathbb{R}^3)$ such that

$$\lim_{n\to+\infty}(\varphi_n,((1-\tilde{\chi})VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1}f) = (w_4, f)\,.$$

For the third term in (47), we have to separate the cases $k=0$ and $k\geq 1$.

Let $k=0$. The terms $R_{\gamma^{\rm HF}}\varphi$ and $K_{\gamma^{\rm HF}}\varphi$ belong to $L^2(\mathbb{R}^3)$, since $R_{\gamma^{\rm HF}} \in L^\infty(\mathbb{R}^3)$ (see (23)) and $K_{\gamma^{\rm HF}}$ is Hilbert-Schmidt (see Lemma 2), and therefore

$$\mathfrak{b}_{\gamma^{\rm HF}}(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})f) = \alpha\,(E(\mathbf{p})\chi E(\mathbf{p})^{-1}(R_{\gamma^{\rm HF}}-K_{\gamma^{\rm HF}})\varphi, f)\,.$$

Assume now $k\geq 1$. With $\tilde{\chi}$ as before,

$$\begin{aligned}\mathfrak{b}_{\gamma^{\rm HF}}(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1}f) &= \alpha\,(\tilde{\chi}(R_{\gamma^{\rm HF}}-K_{\gamma^{\rm HF}})\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1}f) \\ &\quad + \alpha\,((1-\tilde{\chi})(R_{\gamma^{\rm HF}}-K_{\gamma^{\rm HF}})\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1}f)\,.\end{aligned} \tag{50}$$

By the induction hypothesis and Lemma 6 (see Appendix A) we have that $\tilde{\chi}R_{\gamma^{\rm HF}}\varphi$ and $\tilde{\chi}K_{\gamma^{\rm HF}}\varphi$ belong to $H^k(\mathbb{R}^3)$. Therefore there exists $w_5 \in L^2(\mathbb{R}^3)$ such that

$$(\tilde{\chi}(R_{\gamma^{\rm HF}}-K_{\gamma^{\rm HF}})\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1}f) = (w_5, f)\,.$$

For the second term in (50) we find, since $R_{\gamma^{\rm HF}}\varphi,\ K_{\gamma^{\rm HF}}\varphi \in L^2(\mathbb{R}^3)$, that

$$\begin{aligned}&((1-\tilde{\chi})(R_{\gamma^{\rm HF}}-K_{\gamma^{\rm HF}})\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1}f) \\ &\qquad = (\chi E(\mathbf{p})^{-1}(1-\tilde{\chi})(R_{\gamma^{\rm HF}}-K_{\gamma^{\rm HF}})\varphi, E(\mathbf{p})^{k+1}f)\,,\end{aligned}$$

and the result follows since $\chi E(\mathbf{p})^{-1}(1-\tilde{\chi})$ is a smoothing operator. □

2.3. **Exponential decay of the Hartree-Fock orbitals.** The pointwise exponential decay (30) will be a consequence of Proposition 1 and Lemma 4 below.

Proposition 1. *Let $\gamma^{\rm HF}$ be a Hartree-Fock minimizer, let $h_{\gamma^{\rm HF}}$ be the corresponding Hartree-Fock operator as defined in* (25)*, and let $\{\varphi_i\}_{i=1}^N$ be the Hartree-Fock orbitals, such that*

$$h_{\gamma^{\rm HF}}\varphi_i = \varepsilon_i\varphi_i\ ,\ i=1,\dots,N\,,$$

with $0>\varepsilon_N\geq\ldots\geq\varepsilon_1> -\alpha^{-1}$ the N lowest eigenvalues of $h_{\gamma^{\rm HF}}$.

(i) *Let $\nu_{\varepsilon_N} := \sqrt{-\varepsilon_N(2\alpha^{-1}+\varepsilon_N)}$. Then $\varphi_i \in \mathcal{D}(e^{\beta|\cdot|})$ for every $\beta<\nu_{\varepsilon_N}$ and $i\in\{1,\dots,N\}$.*

(ii) *Assume $h_{\gamma^{\rm HF}}\varphi = \varepsilon\varphi$ for some $\varepsilon\in[\varepsilon_N,0)$, and let $\nu_\varepsilon := \sqrt{-\varepsilon(2\alpha^{-1}+\varepsilon)}$. Then $\varphi\in\mathcal{D}(e^{\beta|\cdot|})$ for every $\beta<\nu_\varepsilon$.*

Lemma 4. *Let $E<0$ and $\nu_E := \sqrt{|-E(2\alpha^{-1}+E)|} = \sqrt{|\alpha^{-2}-(E+\alpha^{-1})^2|}$.*

Then the operator $T(-\mathrm{i}\nabla)-E = \sqrt{-\Delta+\alpha^{-2}}-\alpha^{-1}-E$ is invertible and the integral kernel of its inverse is given by

$$\begin{aligned}(T-E)^{-1}(\mathbf{x},\mathbf{y}) = G_E(\mathbf{x}-\mathbf{y}) &= \frac{(E+\alpha^{-1})e^{-\nu_E|\mathbf{x}-\mathbf{y}|}}{4\pi|\mathbf{x}-\mathbf{y}|} + \frac{\alpha^{-1}}{2\pi^2}\frac{K_1(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)}{|\mathbf{x}-\mathbf{y}|} \\ &\quad + (\alpha^{-2}-\nu_E^2)\frac{\alpha^{-1}}{2\pi^2}\Big[\frac{K_1(\alpha^{-1}|\cdot|)}{|\cdot|} * \frac{e^{-\nu_E|\cdot|}}{4\pi|\cdot|}\Big](\mathbf{x}-\mathbf{y})\,,\end{aligned} \tag{51}$$

where K_1 is a modified Bessel function of the second kind [1].

Moreover,

$$0\leq G_E(\mathbf{x}) \leq C_{\alpha,E}\frac{e^{-\nu_E|\mathbf{x}|}}{4\pi|\mathbf{x}|} + \frac{\alpha^{-1}}{2\pi^2}\frac{K_1(\alpha^{-1}|\mathbf{x}|)}{|\mathbf{x}|}\,, \tag{52}$$

$$e^{\beta|\cdot|}G_E \in L^q(\mathbb{R}^3) \quad \textit{for all} \quad \beta<\nu_E \quad \textit{and} \quad q\in[1,3/2)\,. \tag{53}$$

Proof of Lemma 4: The formula (51) for the kernel of $(T-E)^{-1}$ can be found in [16, eq. (35)].

The estimate (52) is a consequence of the bound

$$\frac{K_1(\alpha^{-1}|\cdot|)}{|\cdot|} * \frac{e^{-\nu_E|\cdot|}}{4\pi|\cdot|}(\mathbf{x}) \le C_{\alpha,E}\frac{e^{-\nu_E|\mathbf{x}|}}{4\pi|\mathbf{x}|}\,.$$

This estimate, on the other hand, follows from Newton's theorem (see e. g. [12]),

$$\begin{aligned}&\int_{\mathbb{R}^3}\frac{K_1(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)}{|\mathbf{x}-\mathbf{y}|}\,\frac{e^{-\nu_E|\mathbf{y}|}}{4\pi|\mathbf{y}|}\,d\mathbf{y}\\ &\le e^{-\nu_E|\mathbf{x}|}\int_{\mathbb{R}^3}\frac{K_1(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)}{|\mathbf{x}-\mathbf{y}|}\,\frac{e^{\nu_E|\mathbf{x}-\mathbf{y}|}}{4\pi|\mathbf{y}|}\,d\mathbf{y} \le \frac{e^{-\nu_E|\mathbf{x}|}}{4\pi|\mathbf{x}|}\int_{\mathbb{R}^3}\frac{K_1(\alpha^{-1}|\mathbf{z}|)}{|\mathbf{z}|}\,e^{\nu_E|\mathbf{z}|}\,d\mathbf{z}\,.\end{aligned}$$

The last integral is finite since $\nu_E < \alpha^{-1}$, using the following properties of K_1 (see [6, 8.446, 8.451.6]):

$$K_1(t) \le \frac{1}{|t|} \quad \text{for all} \quad t>0\,, \tag{54}$$

and for every $r>0$ there exists c_r such that

$$K_1(t) \le c_r\frac{e^{-t}}{\sqrt{t}} \quad \text{for all} \quad t \ge r\,. \tag{55}$$

The estimate (53) is a consequence of (52), (54), and (55). □

Before proving Proposition 1, we apply it, and Lemma 4, to prove the pointwise exponential decay, i.e., the estimate in (30).

Proof of Theorem 1 (iii): Fix $i \in \{1,\dots,N\}$. If $Z\alpha < 1/2$ we can rewrite the Hartree-Fock equation (28) as

$$\big(\sqrt{-\Delta+\alpha^{-2}}-\alpha^{-1}\big)\varphi_i = \varepsilon_i\varphi_i + \frac{Z\alpha}{|\mathbf{x}|}\,\varphi_i - \alpha R_{\gamma^{\mathrm{HF}}}\varphi_i + \alpha K_{\gamma^{\mathrm{HF}}}\varphi_i\,. \tag{56}$$

The idea of the proof is to study the elliptic regularity of the corresponding parametrix. By Lemma 4 we find that

$$\varphi_i(\mathbf{x}) = \int_{\mathbb{R}^3}(T-\varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})\big[(\varepsilon_i-\varepsilon_N)\varphi_i + \frac{Z\alpha}{|\cdot|}\,\varphi_i - \alpha R_{\gamma^{\mathrm{HF}}}\varphi_i + \alpha K_{\gamma^{\mathrm{HF}}}\varphi_i\big](\mathbf{y})\,d\mathbf{y}\,.$$

In the case $1/2 \le Z\alpha < 2/\pi$, on the other hand, the operator of which we are studying the eigenfunctions cannot be written as a sum of operators acting on $L^2(\mathbb{R}^3)$ and hence we cannot write directly the equation (28) as in (56). However, since the eigenfunctions are smooth away from the origin we are able to write a pointwise equation for a localized version of φ_i. In fact, let $\chi \in C^\infty(\mathbb{R}^3)$ be such that $0 \le \chi \le 1$ and

$$\chi(\mathbf{x}) = \begin{cases} 1 & \text{if } |\mathbf{x}| \ge 1,\\ 0 & \text{if } |\mathbf{x}| \le 1/2\,,\end{cases}$$

and let, for $R>0$, $\chi_R(\mathbf{x}) = \chi(\mathbf{x}/R)$. We will derive an equation (similar to (56)) for $T(-\mathrm{i}\nabla)(\chi_R\varphi_i)$. Indeed, for every $u \in H^{1/2}(\mathbb{R}^3)$ we have that

$$\begin{aligned}(u, h_{\gamma^{\mathrm{HF}}}(\chi_R\varphi_i)) &= \mathfrak{e}(u,\chi_R\varphi_i) - \alpha^{-1}(u,\chi_R\varphi_i) - \mathfrak{v}(u,\chi_R\varphi_i) + \mathfrak{b}_{\gamma^{\mathrm{HF}}}(u,\chi_R\varphi_i)\\ &= (\chi_R u, h_{\gamma^{\mathrm{HF}}}\varphi_i) + \mathfrak{e}(u,\chi_R\varphi_i) - \mathfrak{e}(\chi_R u,\varphi_i)\\ &\quad + \mathfrak{b}_{\gamma^{\mathrm{HF}}}(u,\chi_R\varphi_i) - \mathfrak{b}_{\gamma^{\mathrm{HF}}}(\chi_R u,\varphi_i)\,.\end{aligned}$$

Note that

$$\mathfrak{e}(u,\chi_R\varphi_i) - \mathfrak{e}(\chi_R u,\varphi_i) = (u,[E(\mathbf{p}),\chi_R]\varphi_i)\,,$$

where $[E(\mathbf{p}), \chi_R]$ is a bounded operator in $L^2(\mathbb{R}^3)$ (see Appendix B), and

$$\mathfrak{b}_{\gamma^{\rm HF}}(u, \chi_R\varphi_i) - \mathfrak{b}_{\gamma^{\rm HF}}(\chi_R u, \varphi_i) = (u, \mathcal{K}\varphi_i)\,,$$

with $\mathcal{K}$ the bounded operator on $L^2(\mathbb{R}^3)$ given by the kernel

$$\mathcal{K}(\mathbf{x},\mathbf{y}) = \alpha\sum_{j=1}^{N}\varphi_j(\mathbf{x})\overline{\varphi_j(\mathbf{y})}\,\frac{\chi_R(\mathbf{x}) - \chi_R(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,. \tag{57}$$

Therefore there exists $w \in L^2(\mathbb{R}^3)$ such that

$$\begin{aligned}\mathfrak{e}(u, \chi_R\varphi_i) = (\varepsilon_i + \alpha^{-1})(u, \chi_R\varphi_i) + \mathfrak{v}(u, \chi_R\varphi_i) - \mathfrak{b}_{\gamma^{\rm HF}}(u, \chi_R\varphi_i)\\ + (u, [E(\mathbf{p}), \chi_R]\varphi_i) + (u, \mathcal{K}\varphi_i) = (u, w)\,.\end{aligned}$$

Hence $\chi_R\varphi_i \in H^1(\mathbb{R}^3)$ and we can write the pointwise equation

$$\begin{aligned}(\sqrt{-\Delta + \alpha^{-2}} - \alpha^{-1})\chi_R\varphi_i = \varepsilon_i\chi_R\varphi_i + \frac{Z\alpha}{|\mathbf{x}|}\chi_R\varphi_i - \alpha R_{\gamma^{\rm HF}}\chi_R\varphi_i\\ + \alpha K_{\gamma^{\rm HF}}(\chi_R\varphi_i) + [E(\mathbf{p}), \chi_R]\varphi_i + \mathcal{K}\varphi_i\,.\end{aligned} \tag{58}$$

This is the substitute for (56) in the case $1/2 \le Z\alpha < 2/\pi$; if $Z\alpha < 1/2$, the proof below simplifies somewhat, using (56) directly.

By Lemma 4, (58) implies that

$$\begin{aligned}\chi_R(\mathbf{x})\varphi_i(\mathbf{x}) = \int_{\mathbb{R}^3}(T - \varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})\big[\frac{Z\alpha}{|\cdot|}\chi_R\varphi_i - \alpha R_{\gamma^{\rm HF}}\chi_R\varphi_i + \alpha K_{\gamma^{\rm HF}}(\chi_R\varphi_i)\\ + (\varepsilon_i - \varepsilon_N)\chi_R\varphi_i + [E(\mathbf{p}), \chi_R]\varphi_i + \mathcal{K}\varphi_i\big](\mathbf{y})\,d\mathbf{y}\,.\end{aligned} \tag{59}$$

We will first show that, for all $R > 0$ and $\beta < \nu_{\varepsilon_N}$,

$$\chi_R\varphi_i e^{\beta|\cdot|} \in L^p(\mathbb{R}^3) + L^\infty(\mathbb{R}^3) \quad \text{for } p \in [2, 6)\,, \tag{60}$$

and then, by a bootstrap argument, that $\chi_R\varphi_i e^{\beta|\cdot|} \in L^\infty(\mathbb{R}^3)$, which is the claim of Theorem 1 (iii).

We multiply (59) by $\chi_{R/2}(\mathbf{x})e^{\beta|\mathbf{x}|}$. Using that $|(Z\alpha/|\mathbf{y}|)\chi_R(\mathbf{y})| \le (Z\alpha)/R$ for all $\mathbf{y} \in \mathbb{R}^3$, (23), (24), and (57) (recall (27), that $\varphi_j \in H^{1/2}(\mathbb{R}^3)$, and (5)) we get, for some constant $C = C_{R,\alpha} > 0$, that

$$\begin{aligned}\big|\chi_R(\mathbf{x})\varphi_i(\mathbf{x})e^{\beta|\mathbf{x}|}\big| \le C\chi_{R/2}(\mathbf{x})e^{\beta|\mathbf{x}|}\int_{\mathbb{R}^3}(T - \varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})\big[|\varphi_i(\mathbf{y})| + \sum_{j=1}^{N}|\varphi_j(\mathbf{y})|\big]\,d\mathbf{y}\\ + \chi_{R/2}(\mathbf{x})e^{\beta|\mathbf{x}|}\Big|\int_{\mathbb{R}^3}(T - \varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})\big([E(\mathbf{p}), \chi_R]\varphi_i\big)(\mathbf{y})\,d\mathbf{y}\Big|\,.\end{aligned} \tag{61}$$

We will show that the first term on the right side of (61) belongs to $L^p(\mathbb{R}^3)$ for $p \in [2, 6)$, and that the second belongs to $L^\infty(\mathbb{R}^3)$. This will prove (60).

The first term on the right side of (61) is a sum of terms of the form

$$h_f(\mathbf{x}) := \chi_{R/2}(\mathbf{x})e^{\beta|\mathbf{x}|}\int_{\mathbb{R}^3}(T - \varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})\,|f(\mathbf{y})|\,d\mathbf{y}\,, \tag{62}$$

with f such that, by Proposition 1, $fe^{\beta|\cdot|} \in L^2(\mathbb{R}^3)$. By Lemma 4 we have, using $e^{|\mathbf{x}|-|\mathbf{y}|} \le e^{|\mathbf{x}-\mathbf{y}|}$, that

$$|h_f(\mathbf{x})| \le C\int_{\mathbb{R}^3} e^{\beta|\mathbf{x}-\mathbf{y}|}G_{\varepsilon_N}(\mathbf{x}-\mathbf{y})e^{\beta|\mathbf{y}|}|f(\mathbf{y})|\,d\mathbf{y}\,.$$

From Young's inequality it follows that $h_f \in L^p(\mathbb{R}^3)$ for all $p \in [2, 6)$, since $\beta < \nu_{\varepsilon_N}$, so (by Proposition 1) $fe^{\beta|\cdot|} \in L^2(\mathbb{R}^3)$ and (by Lemma 4) $e^{\beta|\cdot|}G_{\varepsilon_N} \in L^q(\mathbb{R}^3)$ for all $q \in [1, 3/2)$.

We now prove that the second term on the right side of (61) is in $L^\infty(\mathbb{R}^3)$. This follows from Young's inequality once we have proved that

$$e^{\beta|\cdot|}[E(\mathbf{p}),\chi_R]\varphi_i \in L^p(\mathbb{R}^3) \quad \text{for } p\in[2,\infty)\,, \tag{63}$$

since

$$\begin{aligned} &e^{\beta|\mathbf{x}|}\Big|\int_{\mathbb{R}^3}(T-\varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})\big([E(\mathbf{p}),\chi_R]\varphi_i\big)(\mathbf{y})\,d\mathbf{y}\Big| \\ &\quad\le \int_{\mathbb{R}^3} e^{\beta|\mathbf{x}-\mathbf{y}|}G_{\varepsilon_N}(\mathbf{x}-\mathbf{y})e^{\beta|\mathbf{y}|}\big|[E(\mathbf{p}),\chi_R]\varphi_i\big|(\mathbf{y})\,d\mathbf{y}\,,\end{aligned}$$

and $e^{\beta|\cdot|}G_{\varepsilon_N}\in L^q(\mathbb{R}^3)$ for $q\in[1,3/2)$.

To prove (60) it therefore remains to prove (63). To do so, we consider a new localization function. Let $\eta\in C_0^\infty(\mathbb{R}^3)$ be such that $0\le\eta\le 1$ and

$$\eta(\mathbf{x}) = \begin{cases} 1 & \text{if } R/4\le|\mathbf{x}|\le 3R/2 \\ 0 & \text{if } |\mathbf{x}|\le R/8 \text{ or } |\mathbf{x}|\ge 2R\,, \end{cases}$$

and consider the following splitting

$$\begin{aligned} e^{\beta|\cdot|}[E(\mathbf{p}),\chi_R]\varphi_i &= e^{\beta|\cdot|}\eta[E(\mathbf{p}),\chi_R](\eta\varphi_i) + e^{\beta|\cdot|}\eta[E(\mathbf{p}),\chi_R]((1-\eta)\varphi_i) \\ &\quad + e^{\beta|\cdot|}(1-\eta)[E(\mathbf{p}),\chi_R](\eta\varphi_i) + e^{\beta|\cdot|}(1-\eta)[E(\mathbf{p}),\chi_R](1-\eta)\varphi_i\,. \end{aligned} \tag{64}$$

Since $\eta\varphi_i\in H^k(\mathbb{R}^3)$ for all $k\in\mathbb{N}$ (as proved earlier), $[E(\mathbf{p}),\chi_R](\eta\varphi_i)$ belongs to $H^k(\mathbb{R}^3)$ for all $k\in\mathbb{N}$. Hence, since η has compact support away from $\mathbf{x}=0$, the first term on the right side of (64) is in $L^p(\mathbb{R}^3)$ for $p\in[1,\infty]$ by Sobolev's imbedding theorem (the term is smooth).

For the second term in (64) we proceed by duality: We will prove that

$$\psi(\mathbf{x}) := \big(e^{\beta|\cdot|}\eta[E(\mathbf{p}),\chi_R]((1-\eta)\varphi_i)\big)(\mathbf{x})$$

defines a bounded linear functional on $L^q(\mathbb{R}^3)$ for any $q\in(1,2]$. It then follows that $\psi\in L^p(\mathbb{R}^3)$ for all $p\in[2,\infty)$.

Note that [12, 7.12 Theorem (iv)]

$$\begin{aligned} &(g,[\sqrt{-\Delta+\alpha^{-2}}-\alpha^{-1}]g) \\ &\quad = \frac{\alpha^{-2}}{4\pi^2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{|g(\mathbf{x})-g(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|^2}K_2(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)\,d\mathbf{x}d\mathbf{y} \quad \text{for } g\in\mathcal{S}(\mathbb{R}^3)\,, \end{aligned} \tag{65}$$

where K_2 is a modified Bessel function of the second kind (in fact, $K_2(t) = -t\frac{d}{dt}[t^{-1}K_1(t)]$), satisfying [1]

$$K_2(t)\le Ct^{-1}e^{-t} \quad \text{for } \ t\ge 1\,. \tag{66}$$

Let $f\in C_0^\infty(\mathbb{R}^3)$. Using (65) and polarization, we have that

$$\begin{aligned} &\int_{\mathbb{R}^3}\overline{f(\mathbf{x})}\psi(\mathbf{x})\,d\mathbf{x} = (f, e^{\beta|\cdot|}\eta[E(\mathbf{p}),\chi_R]((1-\eta)\varphi_i)) \\ &= \frac{\alpha^{-2}}{4\pi^2}\iint_{|\mathbf{x}-\mathbf{y}|\ge R/4}\frac{\chi_R(\mathbf{x})-\chi_R(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|^2}\,K_2(\alpha^{-1}|\mathbf{x}-\mathbf{y}|) \\ &\qquad\times\big[\overline{f(\mathbf{x})}e^{\beta|\mathbf{x}|}\eta(\mathbf{x})(1-\eta(\mathbf{y}))\varphi_i(\mathbf{y}) - \overline{f(\mathbf{y})}e^{\beta|\mathbf{y}|}\eta(\mathbf{y})(1-\eta(\mathbf{x}))\varphi_i(\mathbf{x})\big]\,d\mathbf{x}d\mathbf{y}\,, \end{aligned}$$

by the properties of χ and η. Hence,

$$
\begin{aligned}
&\Big|\int_{\mathbb{R}^3}\overline{f(\mathbf{x})}\psi(\mathbf{x})\,d\mathbf{x}\Big| \\
&\qquad\le C_R\iint_{|\mathbf{x}-\mathbf{y}|\ge R/4}|f(\mathbf{x})|e^{\beta|\mathbf{x}-\mathbf{y}|}K_2(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)e^{\beta|\mathbf{y}|}|\varphi_i(\mathbf{y})|\,d\mathbf{x}d\mathbf{y}\,, \\
&\qquad\le C_R\iint|f(\mathbf{x})|e^{\beta|\mathbf{x}-\mathbf{y}|}K_2(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)\chi_{R/4}(|\mathbf{x}-\mathbf{y}|)e^{\beta|\mathbf{y}|}|\varphi_i(\mathbf{y})|\,d\mathbf{x}d\mathbf{y}\,. \quad (67)
\end{aligned}
$$

Note that, since $\beta < \nu_{\varepsilon_N} < \alpha^{-1}$, (66) implies that $e^{\beta|\,\cdot\,|}K_2(\alpha^{-1}|\cdot|)\chi_{R/4}$ is in $L^r(\mathbb{R}^3)$ for all $r\ge 1$. Since (by Proposition 1) $e^{\beta|\,\cdot\,|}\varphi_i\in L^2(\mathbb{R}^3)$, Young's inequality therefore gives that

$$(e^{\beta|\,\cdot\,|}K_2(\alpha^{-1}|\cdot|)\chi_{R/4}) * (e^{\beta|\,\cdot\,|}|\varphi_i|)\in L^s(\mathbb{R}^3) \quad \text{for all } s\in[2,\infty)\,.$$

This, (67), and Hölder's inequality (with $1/q+1/s=1$) imply that, for all $f\in C_0^\infty(\mathbb{R}^3)$ and all $q\in(1,2]$

$$\Big|\int_{\mathbb{R}^3}\overline{f(\mathbf{x})}\psi(\mathbf{x})\,d\mathbf{x}\Big|\le C_R\big\|(e^{\beta|\,\cdot\,|}K_2(\alpha^{-1}|\cdot|)\chi_{R/4}) * (e^{\beta|\,\cdot\,|}|\varphi_i|)\big\|_s\,\|f\|_q\,.$$

By density of $C_0^\infty(\mathbb{R}^3)$ in $L^q(\mathbb{R}^3)$, it follows that ψ defines a bounded linear functional on $L^q(\mathbb{R}^3)$ for any $q\in(1,2]$, and therefore, that $\psi\in L^p(\mathbb{R}^3)$ for all $p\in[2,\infty)$.

Proceeding similarly one shows that the two remaining terms in (64) are also in $L^p(\mathbb{R}^3)$ for all $p\in[2,\infty)$.

This finishes the proof of (63), and therefore of (60).

Finally we prove that $\chi_R\varphi_i e^{\beta|\,\cdot\,|}\in L^\infty(\mathbb{R}^3)$. We start again from (61). We already know that the second term is in $L^\infty(\mathbb{R}^3)$. The first term is a sum of terms of the form (see also (62))

$$h_f(\mathbf{x})=\chi_{R/2}(\mathbf{x})e^{\beta|\mathbf{x}|}\int_{\mathbb{R}^3}(T-\varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})|f(\mathbf{y})|\,d\mathbf{y}\,,$$

with $f\in L^2(\mathbb{R}^3)$ and $\chi_{R/4}e^{\beta|\,\cdot\,|}f\in L^p(\mathbb{R}^3)+L^\infty(\mathbb{R}^3)$ for $p\in[2,6)$ by what just proved, replacing R by $R/4$ in (60). We find that

$$
\begin{aligned}
h_f(\mathbf{x})\le{}&\chi_{R/2}(\mathbf{x})\int_{\mathbb{R}^3}e^{\beta|\mathbf{x}-\mathbf{y}|}(T-\varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})e^{\beta|\mathbf{y}|}\chi_{R/4}(\mathbf{y})|f(\mathbf{y})|\,d\mathbf{y} \\
&+\chi_{R/2}(\mathbf{x})\int_{\mathbb{R}^3}e^{\beta|\mathbf{x}-\mathbf{y}|}(T-\varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})e^{\beta|\mathbf{y}|}(1-\chi_{R/4})(\mathbf{y})|f(\mathbf{y})|\,d\mathbf{y}\,,
\end{aligned}
$$

and, again by Young's inequality, we see that both terms are in $L^\infty(\mathbb{R}^3)$. Notice that in the second integrand $|\mathbf{x}-\mathbf{y}|>R/4$.

This finishes the proof of Theorem 1 (iii). □

It therefore remains to prove Proposition 1.

Proof of Proposition 1: We start by proving (i). It will be convenient to write the Hartree-Fock equations $h_{\gamma^{\mathrm{HF}}}\varphi_i=\varepsilon_i\varphi_i$, $i=1,\ldots,N$, (see (28)) as a system.

Let $\mathtt{t}$ be the quadratic form with domain $[H^{1/2}(\mathbb{R})]^N$ defined by

$$\mathtt{t}(\mathrm{u},\mathrm{v})=\sum_{i=1}^N\mathtt{t}(\mathrm{u}_i,\mathrm{v}_i)\text{ for all }\mathrm{u},\mathrm{v}\in[H^{1/2}(\mathbb{R}^3)]^N\,,$$

where u_i denotes the i-th component of $\mathrm{u}\in[H^{1/2}(\mathbb{R}^3)]^N$ and $\mathtt{t}$ is the quadratic form defined in (7). Similarly we define the quadratic forms $\mathtt{v}$, $\mathtt{r}_\gamma$ and $\mathtt{k}_\gamma$, all with domain $[H^{1/2}(\mathbb{R}^3)]^N$, by

$$\mathtt{v}(\mathrm{u},\mathrm{v}) = \sum_{i=1}^N \mathfrak{v}(\mathrm{u}_i,\mathrm{v}_i)\,, \quad \mathtt{r}_\gamma(\mathrm{u},\mathrm{v}) = \alpha\sum_{i=1}^N (\mathrm{u}_i, R_\gamma \mathrm{v}_i)\,, \quad \mathtt{k}_\gamma(\mathrm{u},\mathrm{v}) = \alpha\langle \mathrm{u}, \mathrm{K}_\gamma \mathrm{v}\rangle\,,$$

with $\mathfrak{v}$ defined in (6), R_γ defined in (22), and K_γ the $N\times N$-matrix given by

$$(\mathrm{K}_\gamma)_{i,j} = \int_{\mathbb{R}^3} \frac{\varphi_i(\mathbf{y})\overline{\varphi_j(\mathbf{y})}}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{y}\,.$$

The effect of writing the Hartree-Fock equations as a system is that K_γ is a (non-diagonal) multiplication operator. This idea was already used in [13]. Note that $(\mathrm{K}_\gamma)_{i,j} \in L^3(\mathbb{R}^3)\cap L^\infty(\mathbb{R}^3)$; the argument is the same as for (22).

Let finally $\mathtt{E}$ be the $N\times N$ matrix defined by $(\mathtt{E})_{i,j} = -\varepsilon_i\delta_{i,j}$.

We then define the quadratic form $\mathtt{q}$ by

$$\mathtt{q}(\mathrm{u},\mathrm{v}) = \mathtt{t}(\mathrm{u},\mathrm{v}) - \mathtt{v}(\mathrm{u},\mathrm{v}) + \mathtt{r}_\gamma(\mathrm{u},\mathrm{v}) - \mathtt{k}_\gamma(\mathrm{u},\mathrm{v}) + \langle \mathrm{u}, \mathtt{E}\mathrm{v}\rangle\,. \tag{68}$$

One sees that the quadratic form domain of $\mathtt{q}$ is $[H^{1/2}(\mathbb{R}^3)]^N$, that $\mathtt{q}$ is closed (since $\mathtt{t}$ is closed), and that there exists a unique selfadjoint operator $\mathtt{H}$ with $\mathcal{D}(\mathtt{H}) \subset [H^{1/2}(\mathbb{R}^3)]^N$ such that

$$\langle \mathrm{u}, \mathtt{H}\mathrm{v}\rangle = \mathtt{q}(\mathrm{u},\mathrm{v}) \quad \text{for all} \quad \mathrm{u}\in [H^{1/2}(\mathbb{R}^3)]^N\,,\ \mathrm{v}\in\mathcal{D}(\mathtt{H})\,.$$

Notice that the vector $\Phi = (\varphi_1,\ldots,\varphi_N)$ satisfies $\mathtt{H}\Phi = 0$.

Let $W(\kappa)$, $\kappa\in\mathbb{C}^3$, denote the multiplication operator from a subset of $[L^2(\mathbb{R}^3)]^N$ to $[L^2(\mathbb{R}^3)]^N$ given by $f(\mathbf{x})\mapsto e^{i\kappa\cdot\mathbf{x}}f(\mathbf{x})$. Instead of proving directly the claim of the proposition, we are going to prove the following statement, which implies the proposition:

$$\Phi\in\mathcal{D}(W(\kappa)) \quad \text{for} \quad \|\mathrm{Im}(\kappa)\|_{\mathbb{R}^3} < \nu_{\varepsilon_N}\,, \tag{69}$$

where $\Phi = (\varphi_1,\ldots,\varphi_N)$. Here, $\kappa = \mathrm{Re}(\kappa) + i\mathrm{Im}(\kappa)$ with $\mathrm{Re}(\kappa),\mathrm{Im}(\kappa)\in\mathbb{R}^3$.

We know that $W(\kappa)\Phi$ is well defined on $[L^2(\mathbb{R}^3)]^N$ for $\kappa\in\mathbb{R}^3$ and we need to show that it has a continuation into the ‘strip’ $\Sigma_{\nu_{\varepsilon_N}}$, where

$$\Sigma_t := \{\kappa\in\mathbb{C}^3 \mid \|\mathrm{Im}(\kappa)\|_{\mathbb{R}^3} < t\}\,.$$

We shall also need $\Sigma_{\alpha^{-1}}$; note that $\Sigma_{\alpha^{-1}}\supset\Sigma_{\nu_{\varepsilon_N}}$. The idea is to use O'Connor's Lemma (see Lemma 5 below).

Starting from the quadratic form $\mathtt{q}$ defined in (68) we define the following family of quadratic forms on $[H^{1/2}(\mathbb{R}^3)]^N$:

$$\mathtt{q}(\kappa)(\mathrm{u},\mathrm{u}) := \mathtt{q}(W(-\kappa)\mathrm{u}, W(-\kappa)\mathrm{u})\,,$$

depending on the *real* parameter $\kappa\in\mathbb{R}^3$. From the definition,

$$\mathtt{q}(\kappa)(\mathrm{u},\mathrm{u}) = \mathtt{t}(\kappa)(\mathrm{u},\mathrm{u}) - \mathtt{v}(\mathrm{u},\mathrm{u}) + \mathtt{r}_\gamma(\mathrm{u},\mathrm{u}) - \mathtt{k}_\gamma(\mathrm{u},\mathrm{u}) + \langle\mathrm{u},\mathtt{E}\mathrm{u}\rangle\,,$$

where

$$\mathtt{t}(\kappa)(\mathrm{u},\mathrm{u}) = \sum_{i=1}^N\int_{\mathbb{R}^3}\big(\alpha^{-2}+\sum_{j=1}^3(p_j-\kappa_j)^2\big)^{1/2}|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p} - \alpha^{-1}\langle\mathrm{u},\mathrm{u}\rangle\,. \tag{70}$$

One sees that $\mathtt{q}(\kappa)$ extends to a family of sectorial forms with angle $\theta<\frac{\pi}{4}$, and that $\mathtt{q}(\kappa)$ is holomorphic in the strip $\Sigma_{\alpha^{-1}}$ (indeed, $\|\mathrm{Im}(\kappa)\|_{\mathbb{R}^3}<\alpha^{-1}$ is needed to assure that the complex number under the square root in (70) has non-negative real part for all $\mathbf{p}\in\mathbb{R}^3$). Moreover, $\mathtt{q}(\kappa)$ is closed. Indeed, it is sufficient to prove that the real part of $\mathtt{q}(\kappa)$ is closed, which will follow from

$$\mathtt{v}(\mathrm{u},\mathrm{u}) + \mathtt{r}_\gamma(\mathrm{u},\mathrm{u}) + \mathtt{k}_\gamma(\mathrm{u},\mathrm{u}) + \langle\mathrm{u},\mathtt{E}\mathrm{u}\rangle \le b\,\mathrm{Re}(\mathtt{t}(\kappa))(\mathrm{u},\mathrm{u}) + K\langle\mathrm{u},\mathrm{u}\rangle\,, \tag{71}$$

with $b<1$, $K>0$ and $\mathrm{Re}(\mathtt{t}(\kappa))$ closed. We now prove (71). We already know that

$$\mathtt{r}_\gamma(\mathrm{u},\mathrm{u}) + \mathtt{k}_\gamma(\mathrm{u},\mathrm{u}) + \langle\mathrm{u},\mathtt{E}\mathrm{u}\rangle \le K'\langle\mathrm{u},\mathrm{u}\rangle \text{ for } K'>0\,. \tag{72}$$

By (8) we find

$$\begin{aligned}\mathtt{v}(\mathrm{u},\mathrm{u}) &\le (Z\alpha)\frac{\pi}{2}\sum_{i=1}^{N}\int_{\mathbb{R}^3}|\mathbf{p}|\,|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p}\\ &\le (Z\alpha)\frac{\pi}{2}R\sum_{i=1}^{N}\Big[\int_{|\mathbf{p}|\le R}|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p}+\int_{|\mathbf{p}|\ge R}|\mathbf{p}|\,|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p}\Big]\,. \end{aligned} \tag{73}$$

Let $\delta > 0$ be such that $Z\alpha\frac{\pi}{2}(1-\delta)^{-1} < 1$. Since

$$\begin{aligned}\mathrm{Re}(\mathtt{t}(\kappa))(\mathrm{u},\mathrm{u}) = \sum_{i=1}^{N}\int_{\mathbb{R}^3}&\Big|\alpha^{-2}+\sum_{j=1}^{3}(p_j-\kappa_j)^2\Big|^{1/2}\cos(\theta(\mathbf{p},\kappa))\,|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p}\\ &-\alpha^{-1}\langle \mathrm{u},\mathrm{u}\rangle\,,\end{aligned}$$

with

$$2\cos^2(\theta(\mathbf{p},\kappa))-1 = \frac{\alpha^{-2}+\sum_{j=1}^{3}(p_j-\mathrm{Re}(\kappa_j))^2-(\mathrm{Im}(\kappa_j))^2)}{|\alpha^{-2}+\sum_{j=1}^{3}(p_j-\kappa_j)^2|}\,,$$

there exists $R > 0$ such that $\cos(\theta(\mathbf{p},\kappa)) \ge (1-\delta)$ for $|\mathbf{p}| > R$. Hence we find that

$$\begin{aligned}\mathrm{Re}(\mathtt{t}(\kappa))(\mathrm{u},\mathrm{u}) &\ge (1-\delta)\sum_{i=1}^{N}\int_{|\mathbf{p}|>R}\Big|\alpha^{-2}+\sum_{j=1}^{3}(p_j-\kappa_j)^2\Big|^{1/2}|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p}\\ &\quad-\alpha^{-1}\langle\mathrm{u},\mathrm{u}\rangle\\ &\ge (1-\delta)\sum_{i=1}^{N}\int_{|\mathbf{p}|>R}(|\mathbf{p}|-C)|\,\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p}-\alpha^{-1}\langle\mathrm{u},\mathrm{u}\rangle\,,\end{aligned}\tag{74}$$

with $C > \|\mathrm{Re}(\kappa)\|_{\mathbb{R}^3}$. The estimate in (71) follows combining (72) with (73) and (74).

The fact that $\mathrm{Re}(\mathtt{t}(\kappa))$ is closed follows from

$$\frac{1}{\sqrt{2}}\sum_{i=1}^{N}\int(|\mathbf{p}|-C)\,|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p} \le \mathrm{Re}(\mathtt{t}(\kappa))(\mathrm{u},\mathrm{u}) \le \sum_{i=1}^{N}\int(|\mathbf{p}|+C)|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p}\,,$$

with $C \ge 2\alpha^{-1}+\mathrm{Re}(\kappa)$.

Hence, $\mathtt{q}(\kappa)$ is an analytic family of forms of type (a) ([9, p. 395]). The associated family $\mathtt{H}(\kappa)$ of sectorial operators is a holomorphic family of operators of type (B) and has domain in a subset of $[H^{1/2}(\mathbb{R}^3)]^N$.

We are interested now in locating the essential spectrum of $\mathtt{H}(\kappa)$. Since K_γ is a Hilbert-Schmidt operator, the essential spectrum of $\mathtt{H}(\kappa)$ coincides with the essential spectrum of the operator associated to

$$\mathtt{t}(\kappa)(\mathrm{u},\mathrm{u})-\mathtt{v}(\mathrm{u},\mathrm{u})+\alpha\,\mathtt{r}_\gamma(\mathrm{u},\mathrm{u})+\langle\mathrm{u},\mathtt{E}\mathrm{u}\rangle\,.$$

Notice that the operator associated to this quadratic form is diagonal. Proceeding as in the proof of $\sigma_{\mathrm{ess}}(h_\gamma) = [0,\infty)$ (Lemma 2), one sees that $\sigma_{\mathrm{ess}}(\mathtt{H}(\kappa)) \subset \sigma_{\mathrm{ess}}(T(\kappa)-\varepsilon_N)$ with $T(\kappa) := \sqrt{\alpha^{-2}+\sum_{j=1}^{3}(p_j-\kappa_j)^2}-\alpha^{-1}$. Hence we find that

$$\sigma_{\mathrm{ess}}(\mathtt{H}(\kappa)) \subset \big\{z\in\mathbb{C}\,\big|\,\mathrm{Re}(z) \ge \sqrt{\alpha^{-2}-\|\mathrm{Im}(\kappa)\|^2_{\mathbb{R}^3}}-\alpha^{-1}-\varepsilon_N\big\}\,.$$

Hence 0, eigenvalue of $\mathtt{H}(0)$, remains disjoint from the essential spectrum of $\mathtt{H}(\kappa)$ for all $\kappa\in\Sigma_{\nu_{\varepsilon_N}}$ (recall that $\Sigma_{\nu_{\varepsilon_N}}\subset\Sigma_{\alpha^{-1}}$) .

Since $\mathtt{H}(\kappa)$ is an analytic family of type (B) [20, p.20] in Σ_{ν_ε}, 0 is an eigenvalue of $\mathtt{H}(0)$ and moreover, 0 remains disjoint from the essential spectrum of $\mathtt{H}(\kappa)$, it follows that 0 is an eigenvalue in the pure point spectrum of $\mathtt{H}(\kappa)$ for all $\kappa\in\Sigma_{\nu_{\varepsilon_N}}$ (reasoning as in [20, page 187]). Let $\mathtt{P}(\kappa)$ be the projection onto the eigenspace corresponding to the eigenvalue 0 of the operator $\mathtt{H}(\kappa)$. Then $\mathtt{P}(\kappa)$ is an analytic function in $\Sigma_{\nu_{\varepsilon_N}}$ and for $\kappa \in \Sigma_{\nu_{\varepsilon_N}}$ and $\kappa_0 \in \mathbb{R}$ we have

$$\mathtt{P}(\kappa+\kappa_0) = W(\kappa_0)\mathtt{P}(\kappa)W(-\kappa_0)\,.$$

Here we used that $W(-\kappa_0)$ is a unitary operator. The result of the lemma follows by applying Lemma 5 below to $\tilde{W}(\theta) := e^{i\theta\kappa\cdot\mathbf{x}}$ with $\kappa \in \mathbb{R}^3$, $\|\kappa\|_{\mathbb{R}^3} = \nu_{\varepsilon_N}$, and $\theta \in \{z \in \mathbb{C}\,|\,|\mathrm{Im}(z)| < 1\}$. Notice that $\tilde{W}(\theta) = W(\theta\kappa)$ and that the projection $\tilde{\mathtt{P}}(\theta) := \mathtt{P}(\theta\kappa)$ is analytic and satisfies $\tilde{\mathtt{P}}(\theta+\theta_0) = \tilde{W}(\theta_0)\tilde{\mathtt{P}}(\theta)\tilde{W}(-\theta_0)$ for $\theta_0 \in \mathbb{R}$.

This finishes the proof of (i).

To prove (ii), we can work directly with the Hartree-Fock equation, since, from (i), the function $K_{\gamma^{\mathrm{HF}}}\varphi$ is exponentially decaying. Therefore, let

$$\mathfrak{q}[u,v] = (u, h_{\gamma^{\mathrm{HF}}}v) - \varepsilon(u,v) \quad \text{for} \quad u,v \in H^{1/2}(\mathbb{R}^3)\,, \tag{75}$$

and note that, by assumption, 0 is an eigenvalue for the corresponding operator (φ is an eigenfunction). Define, for $\kappa \in \mathbb{R}^3$,

$$\begin{aligned}\mathfrak{q}(\kappa)[u,v] &= \mathfrak{q}[W(-\kappa)u, W(-\kappa)v] \\ &= \mathfrak{t}(\kappa)[u,v] - \mathfrak{v}[u,v] + \mathfrak{b}_{\gamma^{\mathrm{HF}}}(\kappa)[u,v] - \varepsilon(u,v)\,,\end{aligned} \tag{76}$$

with $W(\kappa)$ and $\mathfrak{t}(\kappa)$ as before (but now on $H^{1/2}(\mathbb{R}^3)$), see (70), and

$$\mathfrak{b}_{\gamma^{\mathrm{HF}}}(\kappa)[u,v] = \alpha(u, R_{\gamma^{\mathrm{HF}}}v) - \alpha(u, K_{\gamma^{\mathrm{HF}}}(\kappa)v)\,, \tag{77}$$

where

$$K_{\gamma^{\mathrm{HF}}}(\kappa)(\mathbf{x},\mathbf{y}) = \sum_{j=1}^{N} \frac{\varphi_j(\mathbf{x})e^{i\kappa\mathbf{x}}e^{-i\kappa\mathbf{y}}\overline{\varphi_j(\mathbf{y})}}{|\mathbf{x}-\mathbf{y}|}\,. \tag{78}$$

Using (i) of the proposition (exponential decay of the Hartree-Fock orbitals $\{\varphi_j\}_{j=1}^N$) one now proves that (78) extends to a holomorphic family of Hilberts-Schmidt operators in $\Sigma_{\nu_{\varepsilon_N}}$. One can now repeat the reasoning in the proof of (i) to obtain the stated exponential decay of φ.

∎

Lemma 5. ([20, p. 196]) *Let $W(\kappa) = e^{i\kappa A}$ be a one-parameter unitary group (in particular, A is self-adjoint) and let D be a connected region in $\mathbb{C}$ with $0 \in D$. Suppose that a projection-valued analytic function $P(\kappa)$ is given on D with $P(0)$ of finite rank and so that*

$$W(\kappa_0)P(\kappa)W(\kappa_0)^{-1} = P(\kappa+\kappa_0) \text{ for } \kappa_0 \in \mathbb{R} \text{ and } \kappa, \kappa+\kappa_0 \in D\,.$$

Let $\psi \in \mathrm{Ran}(P(0))$. Then the function $\psi(\kappa) = W(\kappa)\psi$ has an analytic continuation from $D \cap \mathbb{R}$ to D.

Appendix A. Some useful lemmata

Lemma 6. *Let Ω be an open subset of $\mathbb{R}^3 \setminus \{0\}$ with smooth boundary and let $f_1, f_2 \in H^k(\Omega)$ for some $k \geq 1$.*

Then the function

$$F(\mathbf{x}) := \int_{\mathbb{R}^3} \frac{f_1(\mathbf{y})f_2(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y}$$

belongs to $C^k(\Omega)$ if $k \geq 2$, while if $k = 1$, it belongs to $W^{1,p}(\Omega)$ for all $p \geq 1$, and hence to $C(\Omega)$.

Proof. We are going to prove the following equivalent statement. If $k \geq 2$, $\chi F \in C^k(\mathbb{R}^3)$ for all $\chi \in C_0^\infty(\Omega)$, while if $k = 1$, $\chi F \in W^{1,p}(\mathbb{R}^3)$ for all $p \geq 1$ and $\chi \in C_0^\infty(\Omega)$.

Fix $\chi \in C_0^\infty(\Omega)$ and take $\tilde{\chi} \in C_0^\infty(\Omega)$ verifying $\tilde{\chi} \equiv 1$ on $\operatorname{supp}\chi$ and such that there is a strictly positive distance between $\operatorname{supp}\chi$ and $\operatorname{supp}(1-\tilde{\chi})$. We write $\chi F(\mathbf{x}) = \chi F_1(\mathbf{x}) + \chi F_2(\mathbf{x})$ with

$$F_1(\mathbf{x}) = \int_{\mathbb{R}^3} \frac{\tilde{\chi}(\mathbf{y}) f_1(\mathbf{y}) f_2(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y} \quad \text{and} \quad F_2(\mathbf{x}) = \int_{\mathbb{R}^3} (1-\tilde{\chi}(\mathbf{y})) \frac{f_1(\mathbf{y}) f_2(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y}\,.$$

The term χF_2 is clearly in $C^\infty(\mathbb{R}^3)$. For the other term we use Young's inequality: if $f \in L^p(\mathbb{R}^3)$ and $g \in L^q(\mathbb{R}^3)$ then

$$\|f * g\|_r \leq C\|f\|_p \|g\|_q \quad \text{with } 1 + \frac{1}{r} = \frac{1}{p} + \frac{1}{q}\,. \tag{79}$$

Moreover, if $1/p + 1/q = 1$ then $f * g$ is continuous (see [24, Lemma 2.1]). Let $\alpha \in \mathbb{N}_0^3$ with $|\alpha| \leq k$. Then

$$|D^\alpha(\chi F_1)(\mathbf{x})| \leq \sum_{\substack{\beta_1+\beta_2=\alpha,\\ \beta_1,\beta_2\in\mathbb{N}_0^3}} |D^{\beta_1}\chi(\mathbf{x})| \Big| \int_{\mathbb{R}^3} \frac{1}{|\mathbf{x}-\mathbf{y}|} D^{\beta_2}(\tilde{\chi} f_1 f_2)(\mathbf{y}) d\mathbf{y} \Big|\,. \tag{80}$$

If $f_1, f_2 \in H^k(\Omega)$, $k \geq 2$, then $D^{\beta_2}(\tilde{\chi} f_1 f_2) \in L^{5/3}(\mathbb{R}^3)$ for all β_2 as in (80). From (79), (80) and $\tilde{\chi}/|\cdot| \in L^{5/2}(\mathbb{R}^3)$ it follows that $D^\alpha(\chi F_1)$ is continuous and, since α is arbitrary, that $\chi F \in C^k(\mathbb{R}^3)$.

If $f_1, f_2 \in H^1(\Omega)$ then $\partial(\tilde{\chi} f_1 f_2) \in L^{3/2}(\mathbb{R}^3)$ and from (79) we get (only) that $\partial(\chi F) \in L^p(\mathbb{R}^3)$ for all $p \geq 1$. It then follows that $F \in W^{1,p}(\Omega)$ for all $p \geq 1$ and therefore (by the Sobolev imbedding theorem) $F \in C(\Omega)$. □

Lemma 7. *Let, for $Z\alpha < 2/\pi$, h_0 be the self-adjoint operator defined in (9), and let $\Lambda_-(\alpha)$ be the projection onto the pure point spectrum of h_0.*

Then the operator $\Lambda_-(\alpha) h_0 \Lambda_-(\alpha)$ is Hilbert-Schmidt.

Proof. Let $\epsilon > 0$ be such that $Z\alpha(1+\epsilon) \leq 2/\pi(1-\epsilon)$. We are going to prove that there exists a constant $M = M(\epsilon)$ such that

$$h_0 \geq \frac{1}{M + 2\alpha^{-1}} P(-\Delta - \frac{C}{|\cdot|})P\,, \tag{81}$$

with $C = Z\alpha(M + 2\alpha^{-1})(1 + 1/\epsilon)$ and $P = \chi_{[0,M]}(T(\mathbf{p}))$. The claim will then follow from (81) since

$$\operatorname{Tr}\big([h_0]_-\big)^2 \leq \frac{1}{(M+2\alpha^{-1})^2} \operatorname{Tr}\big([-\Delta - \frac{C}{|\cdot|}]_-\big)^2 < \infty\,.$$

The last inequality follows since the eigenvalues of $-\Delta - C/|\cdot|$ are $-C^2/4n^2, n \in \mathbb{N}$, with multiblicity n^2.

We now prove (81). For $\epsilon > 0$ and any projection P (with $P^\perp = \mathbf{1} - P$), we have that

$$\begin{aligned} h_0 &= P h_0 P + P^\perp h_0 P^\perp - P\frac{Z\alpha}{|\cdot|}P^\perp - P^\perp \frac{Z\alpha}{|\cdot|} P \\ &\geq P(h_0 - \frac{1}{\epsilon}\frac{Z\alpha}{|\cdot|})P + P^\perp(h_0 - \epsilon\frac{Z\alpha}{|\cdot|})P^\perp\,. \end{aligned} \tag{82}$$

By a direct computation one sees that there exists a constant $M = M(\epsilon)$ such that $T(\mathbf{p}) \geq M$ implies $T(\mathbf{p}) \geq (1-\epsilon)|\mathbf{p}|$ and $T(\mathbf{p}) \leq M$ implies $T(\mathbf{p}) \geq \frac{1}{M+2\alpha^{-1}}(-\Delta)$. Hence, with this choice of M and $P = \chi_{[0,M]}(T(\mathbf{p}))$, (82) implies that

$$h_0 \geq P\big[\frac{1}{M+2\alpha^{-1}}(-\Delta) - (1+\epsilon^{-1})\frac{Z\alpha}{|\cdot|}\big]P + P^\perp\big[(1-\epsilon)\sqrt{-\Delta} - (1+\epsilon)\frac{Z\alpha}{|\cdot|}\big]P^\perp\,.$$

The inequality (81) follows directly by the choice of ϵ. □

Appendix B. Pseudodifferential operators

In this appendix we collect facts needed from the calculus of pseudodifferential operators (ψdo's) (for references, see e.g. [8] or [21]).

Define the standard (Hörmander) symbol class $S^\mu(\mathbb{R}^n)$, $\mu \in \mathbb{R}$, to be the set of functions $a \in C^\infty(\mathbb{R}^n_x \times \mathbb{R}^n_\xi)$ satisfying

$$\left|\partial_x^\alpha \partial_\xi^\beta a(x,\xi)\right| \le C_{\alpha,\beta}(1+|\xi|^2)^{(\mu-|\beta|)/2} \text{ for all } (x,\xi) \in \mathbb{R}^n_x \times \mathbb{R}^n_\xi \,. \tag{83}$$

Here, $\alpha, \beta \in \mathbb{N}^n$ and $|\alpha| = \alpha_1 + \cdots + \alpha_n$. Furthermore, $S^\mu(\mathbb{R}^n) \subset S^{\mu'}(\mathbb{R}^n)$ for $\mu \le \mu'$. We denote $S^\infty(\mathbb{R}^n) = \cup_{\mu\in\mathbb{R}} S^\mu(\mathbb{R}^n)$ and $S^{-\infty}(\mathbb{R}^n) = \cap_{\mu\in\mathbb{R}} S^\mu(\mathbb{R}^n)$. Finally, note that $ab \in S^{\mu_1+\mu_2}(\mathbb{R}^n)$, $\partial_x^\alpha \partial_\xi^\beta a \in S^{\mu_1-|\beta|}(\mathbb{R}^n)$ when $a \in S^{\mu_1}(\mathbb{R}^n), b \in S^{\mu_2}(\mathbb{R}^n)$.

A symbol $a \in S^\mu(\mathbb{R}^n)$ defines a linear operator $A = \mathrm{Op}(a) \in: \Psi^\mu$ ('pseudodifferential operator of order μ') by

$$[\mathrm{Op}(a)u](x) = (2\pi)^{-n} \int_{\mathbb{R}^n} e^{ix\cdot\xi} a(x,\xi)\hat{u}(\xi)\, d\xi \,, \tag{84}$$

where $\hat{u}$ is the Fourier-transform of u. The operator A is well-defined on the space $\mathcal{S}(\mathbb{R}^n)$ of Schwartz-functions; it extends by duality to $\mathcal{S}'(\mathbb{R}^n)$, the space of tempered distributions. Note that for

$$a(x,\xi) = \sum_{0\le|\alpha|\le\mu} a_\alpha(x)\xi^\alpha \tag{85}$$

(with a_α smooth and with all derivatives bounded, i.e., $a_\alpha \in \mathcal{B}(\mathbb{R}^n)$), $A = \mathrm{Op}(a) \in \Psi^\mu$ is the partial differential operator given by

$$[\mathrm{Op}(a)u](x) = \sum_{0\le|\alpha|\le\mu} a_\alpha(x) D^\alpha u(x) \,. \tag{86}$$

Note also that, with $a = a(x)$ and $b = b(\xi)$,

$$[\mathrm{Op}(a)u](x) = a(x)u(x) \quad \text{and} \quad [\widehat{\mathrm{Op}(b)u}](\xi) = b(\xi)\hat{u}(\xi) \,.$$

If $a \in S^\mu(\mathbb{R}^n)$, then $\mathrm{Op}(a)$, defined this way, maps $H^k(\mathbb{R}^n)$ continuously into $H^{k-\mu}(\mathbb{R}^n)$ for all $k \in \mathbb{R}$. Here, $H^k(\mathbb{R}^n)$ is the Sobolev-space of order k, consisting of $u \in \mathcal{S}'(\mathbb{R}^n)$ for which

$$\|u\|^2_{H^k(\mathbb{R}^n)} := \int_{\mathbb{R}^n} |\hat{u}(\xi)|^2(1+|\xi|^2)^k \, d\xi \tag{87}$$

is finite; this defines the norm on $H^k(\mathbb{R}^n)$. We denote

$$H^\infty(\mathbb{R}^n) = \bigcap_{k\in\mathbb{R}} H^k(\mathbb{R}^n) \,, \quad H^{-\infty}(\mathbb{R}^n) = \bigcup_{k\in\mathbb{R}} H^k(\mathbb{R}^n) \,.$$

In particular, symbols in $S^0(\mathbb{R}^n)$ define bounded operators on $L^2(\mathbb{R}^n) = H^0(\mathbb{R}^n)$. Furthermore, operators defined by symbols in $S^{-\infty}(\mathbb{R}^n)$ maps any $H^k(\mathbb{R}^n)$ into $H^\infty(\mathbb{R}^n)$; such operators are called 'smoothing'.

We need to compose ψdo's. There exists a composition # of symbols,

$$\# : S^{\mu_1}(\mathbb{R}^n) \times S^{\mu_2}(\mathbb{R}^n) \to S^{\mu_1+\mu_2}(\mathbb{R}^n) \tag{88}$$

$$(a,b) \mapsto a\#b \,, \tag{89}$$

such that $\mathrm{Op}(a)\mathrm{Op}(b) = \mathrm{Op}(a\#b)$. It is given by

$$(a\#b)(x,\xi) = \frac{1}{(2\pi)^n} \int_{\mathbb{R}^n\times\mathbb{R}^n} e^{-iy\cdot\xi} a(x,\xi-\eta)b(x-y,\eta)\, dyd\eta \,. \tag{90}$$

Here, the integral is to be understood as an oscillating integral.

The symbol $a\#b$ has the expansion

$$a\#b \sim \sum_{\alpha} \frac{i^{-|\alpha|}}{\alpha!} (\partial_x^\alpha a)(\partial_\xi^\alpha b)\,. \tag{91}$$

Here, '$\sim$' means that for all $j \in \mathbb{N}$,

$$a\#b - \sum_{|\alpha|<j} \frac{i^{-|\alpha|}}{\alpha!} (\partial_x^\alpha a)(\partial_\xi^\alpha b) \in S^{\mu_1+\mu_2-j}(\mathbb{R}^n) \tag{92}$$

(recall that $(\partial_x^\alpha a)(\partial_\xi^\alpha b) \in S^{\mu_1+\mu_2-|\alpha|}$). One easily sees that the composition is associative.

Proposition 2. *If $a \in S^{m_1}(\mathbb{R}^n)$, $b \in S^{m_2}(\mathbb{R}^n)$ then the symbol associated to $[\mathrm{Op}(a), \mathrm{Op}(b)]$ belongs to $S^{m_1+m_2-1}(\mathbb{R}^n)$.*

In particular, if $\phi_1, \phi_2 \in \mathcal{B}^\infty(\mathbb{R}^n)$ (the smooth functions with bounded derivatives) with $\operatorname{supp}\phi_1 \cap \operatorname{supp}\phi_2 = \emptyset$ and $a \in S^\mu(\mathbb{R}^n)$, $a(x,\xi) = a(\xi)$, then $\phi_1\#a\#\phi_2 \sim 0$, and so, with $A := \mathrm{Op}(a)$,

$$\phi_1 A \phi_2 = \mathrm{Op}(\phi_1)\mathrm{Op}(a)\mathrm{Op}(\phi_2)$$

is smoothing.

Acknowledgement. *The authors wish to thank Heinz Siedentop for useful discussions. Support from the EU IHP network Postdoctoral Training Program in Mathematical Analysis of Large Quantum Systems, contract no. HPRN-CT-2002-00277, and from the Danish Natural Science Research Council, under the grant Mathematical Physics and Partial Differential Equations, is gratefully acknowledged. TØS wishes to thank the Department of Mathematics, LMU Munich, for its hospitality in the spring of 2007.*

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(Anna Dall'Acqua) Zentrum Mathematik der Technischen Universität München, Boltzmannstrasse 3 D-85748 Garching, Germany.

E-mail address: `dallacqu@ma.tum.de`

(Thomas Østergaard Sørensen) Department of Mathematical Sciences, Aalborg University, Fredrik Bajers Vej 7G, DK-9220 Aalborg East, Denmark.

E-mail address: `sorensen@math.aau.dk`

(Edgardo Stockmeyer) Mathematisches Institut, Universität München, Theresienstrasse 39, D-80333 Munich, Germany.

E-mail address: `stock@math.lmu.de`